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## **Preliminary Process Simulation and Analysis of GMODS: Processing of Plutonium Surplus Materials**

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DEPARTMENT OF ENERGY

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**PRELIMINARY PROCESS SIMULATION AND ANALYSIS OF GMODS:  
PROCESSING OF PLUTONIUM SURPLUS MATERIALS**

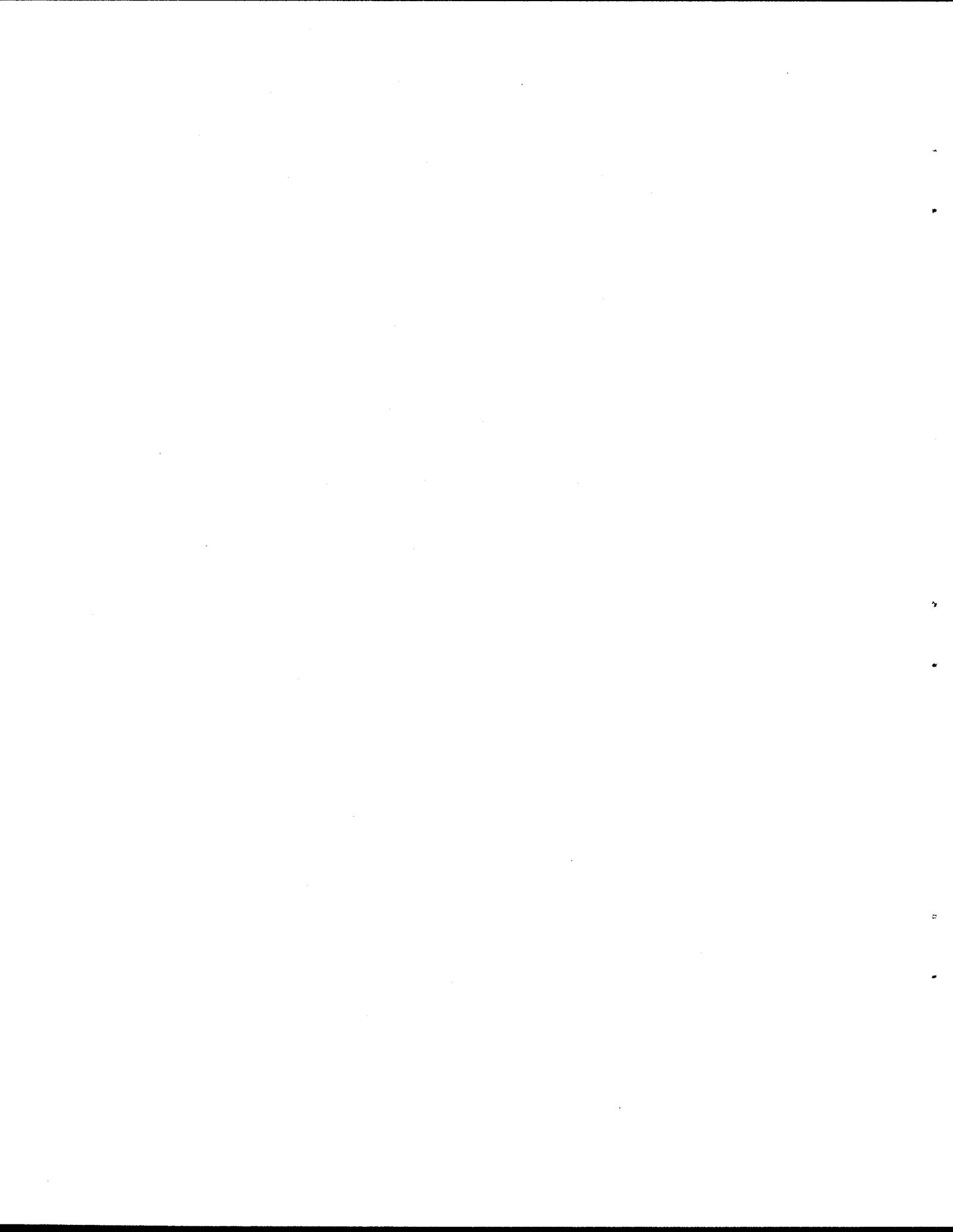
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## ACRONYMS

ANS	American Nuclear Society
CFR	Code of Federal Regulations
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
ES&H	Environment, Safety, and Health
GMODS	Glass Material Oxidation and Dissolution System
GUI	graphical user interface
HLW	high-level waste
IDC	Item Description Code
IDMS	Integrated Defense Waste Processing Facility Melter System
LLNL	Lawrence Livermore National Laboratory
LS	lean scrap
MCC-LP	Materials Characterization Center Static Leach Test
MCC-3	Materials Characterization Center Test No. 3
MO <sub>x</sub>	other oxides
NBO	nonbridging oxygen
NMMSS	Nuclear Materials Management and Safeguards System
ORNL	Oak Ridge National Laboratory
PbO	lead oxide
PCM	plutonium-containing material
PCT	Product Consistency Test
Pu	plutonium
R&D	research and development
RFETS	Rocky Flats Environmental Technology Site
RS	rich scrap
RXNSIADD	reactions and silicon addition
SFM	surplus fissile material
SRL	Savannah River Laboratory
SRS	Savannah River Site
SS&C	sand, slag, and concrete
TCLP	Toxicity Characteristic Leaching Procedure

## **FLOWsheet ABBREVIATIONS**

<b>Pu_Feed</b>	Blends the wastes and feeds the composite stream to the FLOWsheet
<b>CHECKPU</b>	Looks ahead to see if the final glass product will contain too much plutonium and terminates the simulation if the limit is exceeded.
<b>PBO_B_VA</b>	Adds PbO and B <sub>2</sub> O <sub>3</sub> .
<b>RXNSIADD</b>	Oxidizes the waste metals and organics, and calculates how much silicon dioxide (SiO <sub>2</sub> ) must be added to form the desired glass.
<b>NaOH_Scrub_Offgas</b>	Gas cleaning system. It also recovers lead hydroxide.
<b>GLASSFORM</b>	Calculates the amount of SiO <sub>2</sub> that must be added to the melt to maximize the glass loading.

## EXECUTIVE SUMMARY

To address growing concerns in the areas of arms control, control of fissile materials, waste management, and environment and health, the U.S. Department of Energy is studying and evaluating various options for the control and disposal of surplus fissile materials (SFMs). One of the options under consideration is the Glass Material Oxidation and Dissolution System (GMODS). This is a new process developed at Oak Ridge National Laboratory (ORNL). GMODS directly converts plutonium-bearing materials such as metals, ceramics, and organics into a durable-high-quality glass storage or waste form.

This study undertook the development of a computer simulation of the GMODS process using FLOW, a chemical process simulator developed at ORNL. That computer simulation was used to perform an assessment of how GMODS would handle the treatment of plutonium, rich scrap (RS) and lead scrap (LS), and identify critical process parameters. Among the key process parameters affecting the glass formation were processing temperatures, additives, and the effects of varying them on the final product. This assessment looked at the quantity of glass produced, the quality of the final glass form, and the effect of blending different groups of the feed streams on the glass produced. The model also provided a way to study the current process assumptions and determine in which areas more experimental studies are required.

The methodology for determining the formulation and quality of the final waste forms was based on work done for borosilicate glasses at Clemson University and in conjunction with Savannah River Laboratory (SRL). High-quality glass compositions can be mapped as a region on a glass-phase diagram. The glass-formation model in the computer simulation of the GMODS process is divided into two parts. The first part determines whether the glass formed falls within the acceptable region of the glass-phase diagram to ensure a high-quality glass. The second part analyzes properties of the molten glass such as viscosity and modifies the glass by adding additional glass formers or by changing the process temperature to bring these properties to acceptable levels to meet process requirements.

Evaluation of the treatment of the rich and lean scrap waste streams shows that the GMODS process is able to treat both streams separately or combined to form durable glass waste forms. In addition, other tests showed that combining various parts of the two waste streams, such as ashes and chloride salts, can lead to volume reductions of up to 50% compared to treating the two streams separately.

This study showed that the major process parameter affecting the final glass volume is the temperature of the melt when operating within a given viscosity to meet process requirements. For example, when 1 kg of chloride salts was processed, the temperature was at 1103°C and produced 6.5 kg of glass at a given viscosity. However, when the temperature was increased to 1167°C, the final glass mass decreased to about 3 kg at the same viscosity. Fewer additives were required to assure acceptable glass viscosities during processing. A complete set of results is presented in Appendix D, which includes tables showing glass compositions for various rich and lean plutonium (Pu) scrap and residue waste streams as a function of the process temperature. The composition of

the various waste streams are presented in Appendix B. These tables have been compiled from several public reports and heuristics when information was not directly available.

In summary, the simulation of the GMODS process showed that the glass chemistry postulated in the models is workable. It is expected that the glass chemistry assumed during the modeling process can be verified by the results of the laboratory experiments that are currently being conducted relating to the GMODS process. Further waste characterization, especially of the SFM waste streams not studied in this report, will provide more nearly accurate results and give a more detailed evaluation of the GMODS process.

This initial assessment shows that the GMODS process works within an acceptable level of confidence based on similar glass processes used for high-level waste (HLW). Furthermore, GMODS could treat the SFM waste streams, and it can be forecasted that the process has the potential to reduce costs due to its simplicity and flexibility for treating different types of wastes.

# 1. INTRODUCTION

## 1.1 BACKGROUND

The U.S. Department of Energy's (DOE) Fissile Material Disposition Program is evaluating long-term options for surplus fissile materials (SFMs) control and disposition. The evaluations are based on technical, nonproliferation, environmental, budgetary, and economic considerations. The objectives of the program include (1) strengthening national and international arms control efforts by reduced availability of surplus material and (2) ensuring compliance with environment, safety, and health (ES&H) standards. Alternatives being considered include use as fuel in nuclear reactors, short-term storage, immobilization and isolation in a geologic repository, and long-term storage. The Glass Materials Oxidation and Dissolution System (GMODS) process would immobilize SFM in a durable glass for long-term storage or as a first step for disposal as a waste.

The GMODS is a new process<sup>1</sup> that (1) directly converts metals, ceramics, and amorphous solids to glass; (2) oxidizes organics and solidifies their residues into glass; and (3) converts chlorides to low-chloride borosilicate glass and a secondary, clean sodium chloride stream. A batch of feed materials is introduced into a melt of lead-borate glass that oxidizes and dissolves this feed into the glass. The lead oxide in the glass is the oxidant. Oxidation of metals yields metal oxides that dissolve into glass. By-product lead forms a separate layer at the bottom of the melter. Glass formers and other compounds are added to produce a glass with the desired processing and performance properties. Excess lead oxide (PbO) is reduced to lead metal with carbon. The lead is later oxidized and recycled to process the next batch of feed

Several recent publications<sup>2,3</sup> describe the process in detail. Recent experimental results demonstrate that greater than 20 wt %  $UO_2$  + 20 wt %  $ZrO_2$  can be dissolved in lead-borate glass and that uranium (plutonium surrogate), Zircaloy-2, aluminum, cerium (plutonium surrogate), and stainless steel are readily oxidized and converted to glass.

GMODS directly converts plutonium-containing materials (PCMs) into glass. GMODS has a number of advantages when it is compared to other vitrification processes:

- (1) This oxidation-dissolution vitrification process can dissolve the variety of materials found in surplus fissile materials (SFMs)—oxides, metals, and organics.
- (2) Preconditioning steps are not required, thus simplifying operations.
- (3) The main steps of the process are carried out in one vessel, reducing capital costs.
- (4) Process materials such as PbO are recycled or incorporated into the product.
- (5) Solid and liquid waste streams are nil; and
- (6) A high-quality, tailored glass product is formed.

## 1.2 OBJECTIVES

This report presents a preliminary assessment of the GMODS process flowsheet using FLOW, a chemical process simulator developed by Oak Ridge National Laboratory (ORNL).<sup>4</sup> The objectives of this work included the following: (1) to develop a process simulation model to direct research and development (R&D), initiating process design and undertaking performance studies; (2) to evaluate glass product quality for a variety of PCMs; (3) to identify potential waste blends that can produce desirable glass products; and (4) to provide a formal, disciplined method to explicitly identify all flowsheet assumptions.

GMODS was modeled using FLOW, which is particularly well-suited for preliminary analysis of innovative and novel concepts. In this case, the FLOWsheet models were based on the best experimental and theoretical information available when they were created. Assumptions and limitations of the models are described in the modeling section of this report.

The following section summarizes the characteristics of the plutonium-containing feed materials that form the basis for this study. Key issues and limitations with feed materials are identified. Section 3 describes the GMODS process, how and why it works, some requirements for plant operation, and conditions needed to produce high-quality glass. In Sect. 4, general aspects of glass production are analyzed. These aspects are applied in this GMODS modeling effort. Then in Sect. 5, the GMODS process is translated into a process model and applied. Simulation results obtained with these FLOWsheet models are presented in Sect. 6. Conclusions and recommendations are made in Sect. 7. References are cited in Sect. 8. The characterization of the waste streams are shown in Appendix A, and information on calculating glass durability is found in Appendix B. Appendix C shows several of the important data files used in this computer model. Appendix D presents detailed graphics of some of the results, and Appendix E presents a summary of the features of FLOW.

## 2. PLUTONIUM-CONTAINING FEED MATERIAL

### 2.1 GMODS FEED STREAMS

Input data required for the process simulation and analysis of the GMODS process include quantities, composition, chemical characteristics, and the chemical forms of the various waste streams to be treated. The waste streams used in this report are from the *Pretreatment Process for Immobilization Initial Report* by Lawrence Livermore National Laboratory (LLNL). The LLNL report was written as part of the SFM Control and Disposition Program. The information for it was obtained from the Nuclear Materials Management and Safeguards System (NMMSS) database and from the DOE sites.

Using the same categories as listed in the LLNL report<sup>5</sup> the waste stream data were broken into 11 separate feed streams. These feed streams correspond to the 11 major material categories that are typically used in the DOE complex. These categories and a description of each one are listed below.

1. Pits: Any plutonium weapon component or assembly having a serial number or other identification number.
2. Clean plutonium metal: Essentially pure plutonium metal that meets weapons specifications, usually <100 ppm of any impurity. The plutonium can be weapons grade, fuels grade, or reactor grade. The metal may have oxidation or casting residues on the surface.
3. Impure plutonium metal/alloys: Plutonium-bearing metal/alloy that does not meet weapons specifications for chemical purity and will require processing for use as weapons-specification material or may possibly require processing for use in some disposition options.
4. Clean oxide: Oxidized plutonium containing less than 3 wt % impurities.
5. Impure oxide: Oxidized plutonium containing 3–50 wt % impurities.
6. Plutonium compounds (other than oxides): Plutonium compounds and mixtures containing fluorides, carbides, chlorides, etc.
7. Rich scrap (RS): Plutonium-bearing material that primarily contains nonplutonium elements and/or compounds. Material in this category is generally greater than 2 wt % plutonium.
8. Lean scrap (LS): Plutonium-bearing material that contains mostly nonplutonium elements and/or compounds. Material in this category is generally less than 2 wt % plutonium.
9. Unirradiated reactor fuel: Plutonium-bearing reactor fuel that has been manufactured but not irradiated. Unirradiated reactor fuel contains materials in several chemical forms.

10. **Irradiated fuel:** Plutonium-bearing material that meets the definition of "spent nuclear fuel" in the *Code of Federal Regulations* (CFR), 40 CFR Part 191.02. This type of spent fuel contains material in several chemical forms.
11. **Miscellaneous:** Any materials that do not fit any of the above categories. The majority of this material comes in the form of experimental capsules, elements, and pins.

## **2.2 QUANTITIES AND COMPOSITION OF FEED STREAMS**

After the waste feed is divided into its 11 major feed categories, each of these categories must be further sorted into subcategories which better define what is in each feed stream. In the LLNL report,<sup>5</sup> five of the major categories are divided into these subcategories: impure metal/alloys, rich scrap, lean scrap, impure oxide, and miscellaneous. However, the LLNL report gives no information on the total amount of wastes in any of the 11 feed streams or on the percentage breakdown of the waste streams into their various subcategories.

While there is no information on total waste stream quantities in the LLNL report, it does give the amount of RS and LS located at the Rocky Flats Environmental Technology Site (RFETS). It also reports the amount of waste in each of the subcategories for these two waste streams. A breakdown of these two streams is shown in Table A.1 in Appendix A. While this is not all the RS or LS in the DOE complex, it does present a good indication of the type of wastes to be found in these two streams. Because this was the best information available at the time, it was decided that the initial process simulation and analysis of the GMODS process would be done using the RFETS RS and LS data.

## **2.3 WASTE-FEED CHARACTERIZATION**

To use the waste stream data in the FLOW model, the wastes must be described according to their chemical forms. Characterization data for the waste streams studied was found in a RFETS report on residue item description codes (IDC).<sup>6</sup> This report did not give a description of each subcategory in terms of weight percent of each constituent, and it gave only a brief overview of the type of constituents that might be found for each of the waste categories. We used this information to determine a rough characterization of each of the waste subcategories for RS and LS. This information was put into a synonym table (Table A.2 in Appendix A) which was used to convert the waste descriptors into chemical elements for use in the model.

## **2.4 MODELING WASTE FEED BLENDING**

To perform a FLOW analysis of the effect of mixing different waste streams on glass formation, a feed-blending process was specifically computer-coded for the model. With this process the user can blend any of the 11 feed streams that will be sent to the GMODS process. For example, the user can combine 50 wt % of the RS stream with 10 wt % of the clean oxide stream and see the effects on the

final glass quality and quantity. Because only RS and LS were analyzed in this study, the feed-blending process was extended down one more level of detail. That is, the user could set the percentage of each of the RS and LS substreams that were to be fed into the GMODS process. This allowed several studies of the effects on final glass volume and composition resulting from combining parts of two or more substreams to form the process feed. The results from these studies are presented in Sect. 6.

### 3. THE GMODS PROCESS

#### 3.1 PROCESS OVERVIEW

In the GMODS process a lead oxide (PbO)-boron oxide ( $B_2O_3$ ) melt oxidizes and dissolves feed material in a batch melter, thus producing a high-quality glass product. Lead is reduced and precipitated from the melt before the glass product is poured; this is followed by reoxidation and recycle into the melt as makeup PbO for the next batch of feed. Figure 3.1 shows the key GMODS process steps as outlined by Forsberg et al.<sup>3</sup> All process operations are performed in sequence in an induction furnace. GMODS can process metals, oxides, and organics, in a five-step process that follows the startup:

**Startup.** The melter is filled with molten lead-borate glass having a PbO-to- $B_2O_3$  mole ratio of 2 or more.

**Step 1—Feed and oxidize plutonium-containing materials (PCMs).** PCMs are fed to the molten lead-borate glass bath. Metals in the feed react with the lead oxide, forming metal oxides and lead metal. The metal oxides in the feed and form from reactions with PbO directly into the glass. Boron oxide promotes rapid dissolution of metal oxides, including the protective oxide layers that develop on metals. Organics are oxidized to carbon oxides and steam, and PbO is reduced to lead metal. The lead forms a metal layer on the bottom of the melter. High-density feed material (plutonium or uranium metal), which falls to the bottom, dissolves in the lead metal; is oxidized by the lead oxide at the glass-metal interface; and is extracted as oxides into the glass.

**Step 2—High-quality glass formation and excess PbO removal.** Glass additives such as silicon oxide are fed to the melter to produce a lead borosilicate glass. Carbon is also fed to reduce the excess PbO producing carbon dioxide ( $CO_2$ ) and lead metal that drops to the bottom of the smelter.

The GMODS process separates halogens from the waste material being treated and allows production of a nonhalogen high-durability waste form. A reaction occurs between the waste containing chlorides and the sacrificial oxide (PbO) to yield lead chloride, which is a gas at the temperature of the molten glass, and an oxide of the chloride, for example  $Na_2O$ , in the feed which is soluble in the molten glass.

**Step 3—Pour glass.** The product borosilicate glass is poured from the melter into a cylinder or converted into marbles.

**Step 4—Makeup  $B_2O_3$  and PbO.**  $B_2O_3$  and PbO are added to replace the materials that have gone into the glass product.

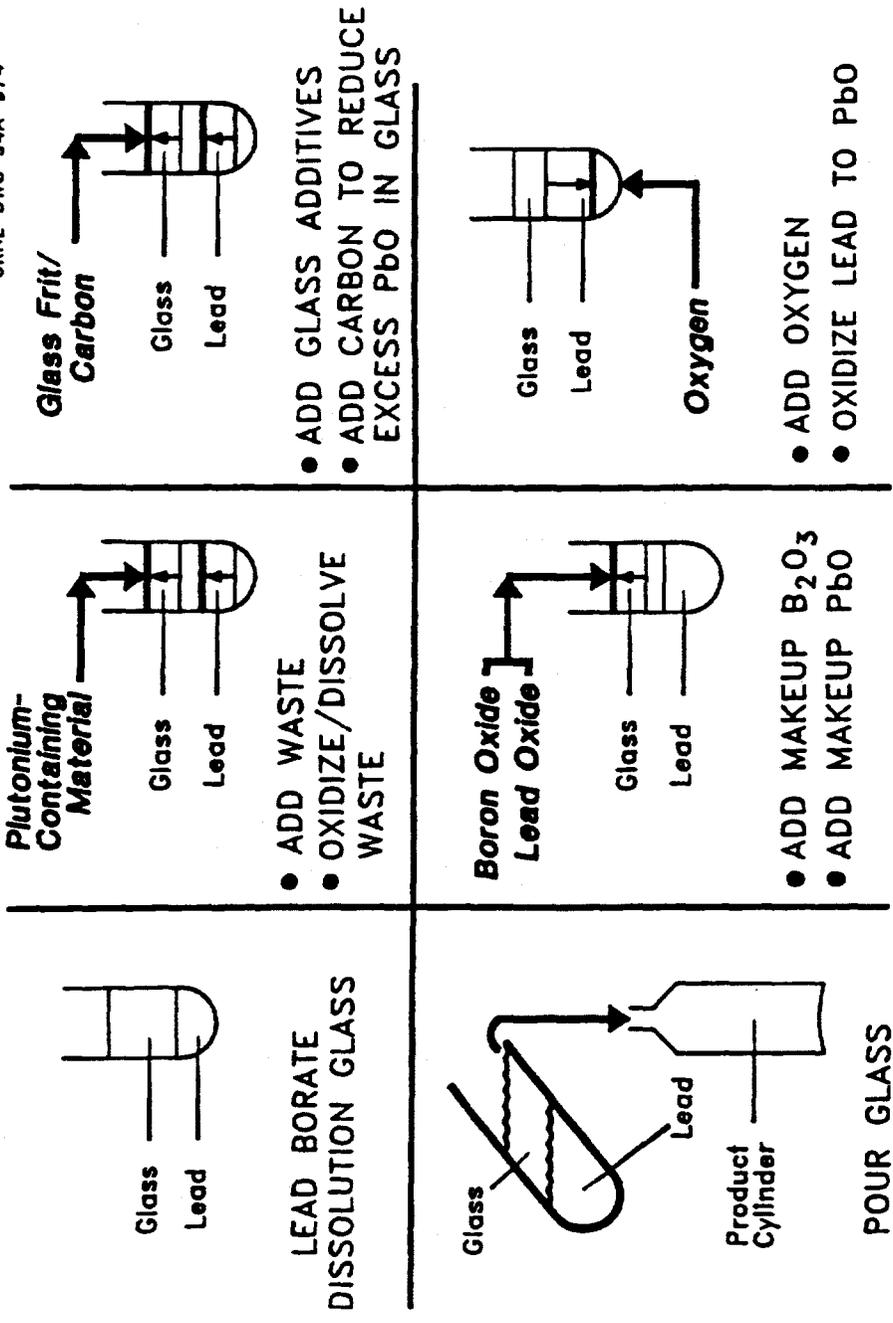


Fig. 3.1. GMODS batch processing of PCM to borosilicate glass.

Step 5—Oxidize lead. Oxygen is introduced to oxidize the lead at the bottom of the melter, thus forming a lead-borate dissolver glass ready for a new batch of feed.

### 3.2 THE REACTIONS DURING THE GMODS PROCESS

Molten lead-borate glass dissolves oxides, as do conventional molten glasses, but the GMODS glass also reacts with metals and organics, for example:



After lead borosilicate glass is formed, excess PbO in the glass is removed by adding carbon, which reacts according to the reactions shown above.

The ability of the PbO-B<sub>2</sub>O<sub>3</sub> system to oxidize metals and to dissolve metal oxides is indicated by the PbO and B<sub>2</sub>O<sub>3</sub> thermochemical activity. Free energy data for ternary PbO-B<sub>2</sub>O<sub>3</sub>-metal oxide systems were not available at the time of this study. However, the oxidation potential of metals are available, and it provides a guide to the treatability of a material by GMODS. Metal oxides with high oxygen potential can oxidize metals with lower potentials. The metals Sn, Fe, Zn, Cr, U, Pu, and Al have lower potential than Pb. Silver, gold, platinum, and copper do not form stable oxides at high temperatures. Therefore, these materials dissolve into the lead. If the concentration of noble metals become significant, standard lead-smelting technology is available for separating noble metals from lead.

### 3.3 PREPARATION OF THE GMODS PROCESS FOR SIMULATION

The essential ingredients for simulating the glass process are the integration of the GMODS process chemistry, the requirements for production of glass, and the application of the FLOW modeling tools. In Sect. 4 the requirements for the production of the desired glass are discussed. In Sect. 5 the modeling tools and the integration of the different elements for the simulation are discussed.

## 4. FACTORS DETERMINING THE PRODUCTION OF A DURABLE GLASS

This section summarizes the procedure for determining the quantity and composition of glass additives for producing a durable glass. The methodology to formulate and predict glass quality was based on work done at Clemson University in conjunction with the Savannah River Laboratory (SRL)<sup>7</sup> for the development of HLW glasses for the Defense Waste Processing Facility (DWPF). In this initial analysis we have assumed that the performance of the plutonium glass should be equivalent to a HLW glass. Glass formulations must consider two key factors in vitrification processes: product quality and processability. Glass-forming compounds are added to the melt to obtain the desired glass properties. Sometimes trade-offs must be made between product-quality attributes and properties that relate to processability when glass compositions are formulated. The high-quality glass compositions can be mapped as a region in the glass-phase diagram. The most important factors for determining process ability are the viscosity and liquidus temperature of the melt.

### 4.1 GLASS QUALITY

By *quality* we mean the long-term performance and durability of the glass necessary for it to perform its role as a matrix for immobilizing radionuclides. The durability of a glass, measured by silicon release rates and constituent leach rates, is a key factor in determining glass quality. The ternary phase diagram for  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-other oxides (R}_2\text{O)}$  (see Fig. 4.1) shows an elliptical region (known as Homogenous Waste Glass Region) in which glasses have acceptable performance characteristics. This subsection describes some of the considerations for formulating glass waste forms in this desirable region. The FLOW module that accomplishes this is described in Sect. 5.3.

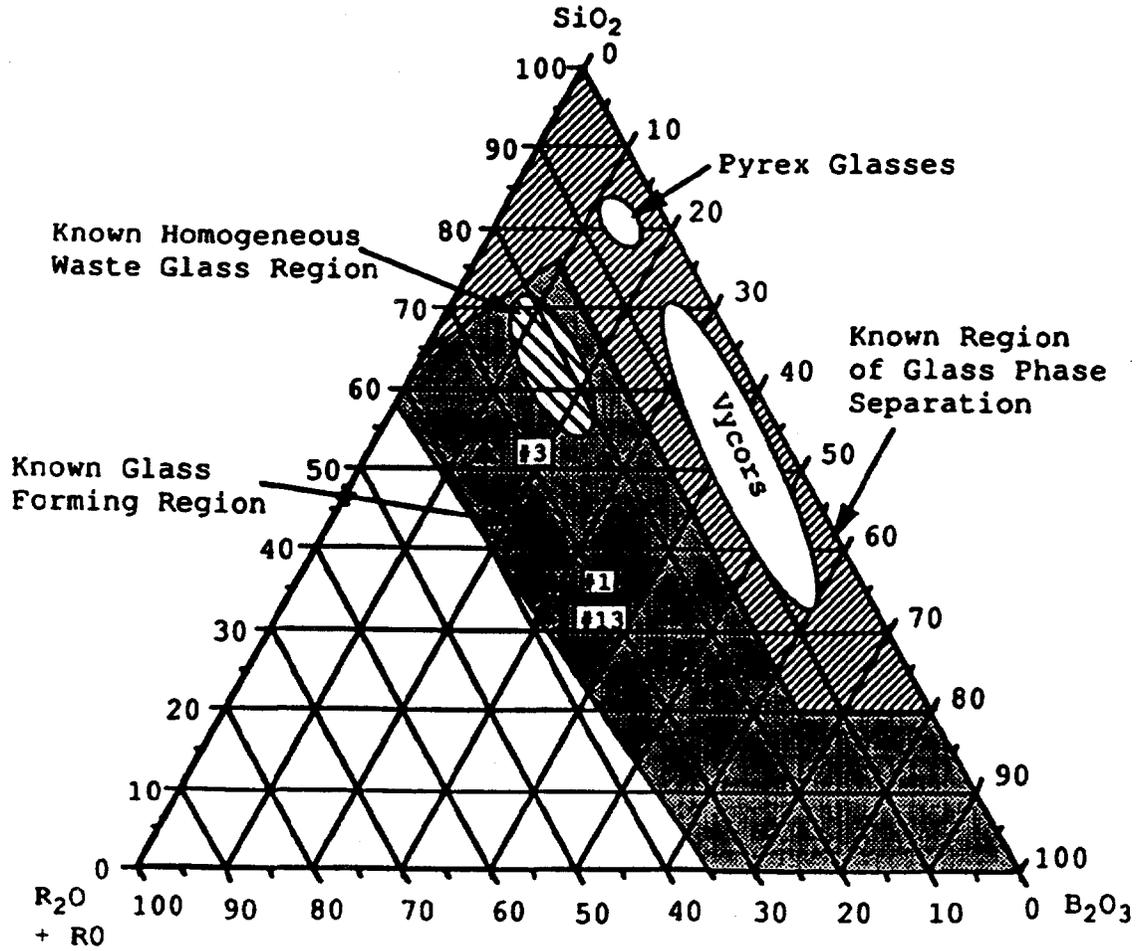
Product durability is associated with the chemical and physical properties of waste glasses including chemical immobilization, physical durability, and devitrification. These properties are closely interrelated to and result from the structural characteristics of glass. Among these properties, the single most important characteristic of waste glass is chemical immobilization, or the ability to resist leaching of the immobilized contaminants when contacted by water or other liquids. In this study only the chemical immobilization was considered.

There are many leaching test methods. They differ in the form of glass, test duration, procedure, etc. The most often applied methods include:

1. Toxicity Characteristic Leaching Procedure (TCLP)
2. Materials Characterization Center Static Leach Test (MCC-LP)
3. Materials Characterization Center Test No. 3 (MCC-3)
4. Product Consistency Test (PCT)
5. American Nuclear Society (ANS) Leach Test (ANS-16.1, 1986)

Three empirical correlations that predict the chemical durability of glass based on different leach test procedures are described in Appendix B.

**Borosilicate Ternary System**



**Fig. 4.1 The ternary phase diagram for  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-R}_2\text{O}$ .**

## 4.2 PROCESSIBILITY

Processibility is represented by those factors that allow a smooth production of glass. The most important factors for determining processibility are the viscosity and liquidus temperature of the melt. Liquidus temperature is defined below.

**4.2.1. Viscosity.** Viscosity is a function of temperature and determines the rate of melting of the raw feed, the rate of glass-bubble release, and the rate of homogenization. If the viscosity is too high, the mixing time to produce homogenous glasses is excessive and any gases that are released may cause foaming in the melter. In general, a viscosity range of 20–500 poise is acceptable frit (material used as the basis for glass production) for the final glass (Note: The lead borate oxidation-dissolution glass has a much lower viscosity than the final glass); a conservative range of 20–100 poise at 1150°C, however, was used for the DWPF at the Savannah River Site (SRS).

The approach to predicting the viscosity was based on glass structural considerations, expressed as a calculated nonbridging oxygen (NBO) term.<sup>8</sup> Calculation of the NBO term from the glass composition was combined with quantitative statistical analyses of response surfaces to express glass viscosity as a function of melt temperature and glass composition. The NBO parameter is representative of the amount of structural depolymerization in the glasses and can be calculated by:

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

where

$$M_2O = Na_2O + K_2O + Cs_2O + Li_2O. \quad (2)$$

$M_2O$ ,  $Fe_2O_3$ ,  $Al_2O_3$ ,  $B_2O_3$ , and  $SiO_2$  are concentrations in weight percent oxides.

Regression analysis of the calculated NBO term with the viscosity,  $\eta$ , yields:

$$\log \eta \text{ (poise)} = -0.61 + \frac{4472.45}{T(C)} - 1.534 NBO \quad (3)$$

where,

$T(C)$  is melting point in degrees Celsius.

**4.2.2. Liquidus.**<sup>9</sup> The liquidus defines the highest temperature at which spinel,<sup>\*</sup> with or without nepheline,<sup>\*\*</sup> crystallizes, e.g. the lowest melter temperature achievable without spinel crystallization. The glass formulations must have a liquidus below the minimum design temperature of the melter (i.e., 1050°C for a DWPF glass melter; the minimum design temperature is the temperature that gives acceptable viscosity). The liquidus temperature was determined 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:



The liquidus was determined by the following equation from regression analysis:

$$\text{Liquidus (C)} = 803.6 + 2277 \kappa, \quad (4)$$

where

$$\kappa = \frac{\text{Fe}_2\text{O}_3(-134 \text{ kcal/mol})}{\text{SiO}_2(-156 \text{ kcal/mol}) - \text{Al}_2\text{O}_3(-360 \text{ kcal/mol})} \quad (5)$$

where  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  are weight percent oxides.

### 4.3 ACCEPTANCE CRITERIA

An example of acceptance criteria used by SRS in the DWPF product composition control system is shown in Table 4.1. The GMODS process will have a similar acceptance criteria table. However, values of these parameters are not yet available experimentally. Consequently, the acceptance criteria to be utilized by the GMODS process may vary from the following values:

Processibility:      Liquidus temperature  $\leq 1050^\circ\text{C}$ .  
                                $20 \leq$  melt viscosity  $\leq 100$  poise.

Acceptability:      Leach rate  $\leq 1 \text{ g/m}_2/\text{d}$ .

(Note that in the literature, there is no description for the leaching test procedure or the basis of the leach rate.)

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\* Spinel is a mineral of magnesium aluminum oxide,  $\text{MgAl}_2\text{O}_4$  having octahedral crystals.

\*\* Nepheline is a feldspathoid mineral, sodium potassium aluminum silicate ( $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$ ).

**Table 4.1 Glass acceptance criteria**

Glass property	Acceptable range
Liquidus (°C)	≤1050
Viscosity (poise)	20–100
Durability (kcal/mol)	$\Delta G_{hyd} \geq -7.0$
TiO <sub>2</sub> (wt %)	≤1.0
Cr <sub>2</sub> O <sub>3</sub> (wt %)	≤3.0
P <sub>2</sub> O <sub>5</sub> (wt %)	≤0.3
Fe <sup>+2</sup> /Fe <sup>+3</sup>	0.1–0.5

## 5. GMODS MODELING WITH FLOW

This section describes FLOW, the modeling package used to conduct this study. Also described are the physical, chemical, and operating concepts of GMODS and how they were translated into a FLOW process model.

### 5.1 INTRODUCTION TO FLOW

FLOW calculates the material flows of process streams by sequentially simulating the chemical and physical behavior of the process unit operations. FLOW includes a wide range of unit operation models. However, in most complex simulations, new user-created models are required. FLOW provides several routes for creating new user models—programming in FORTRAN, C, C++, or Python to create a new independent module, or by combining already existing modules. FLOW features several modules that help estimate the behavior of components when physical properties are not known. For example, with the group separator, chemical groups rather than chemical compounds can be processed. This feature is very handy when property data are not available or when the feed material is not well characterized. The user also has a great deal of flexibility in naming stream constituents. FLOW supports a hierarchical nesting of flowsheets, a feature called aggregation. Thus, one can start with a top-level picture of the process and work toward adding the detail at lower levels, or, conversely, one can start with details that are known to build up a system model. FLOWsheets are easy to put together in FLOW's graphical user interface (GUI) by dragging, dropping, and connecting icons.

#### 5.1.1 FLOW's Analysis

Although commercial software is available that simulates chemical processes, for example, ASPEN™ and CHEMCAD™, these packages tend to emphasize the unit operations and material properties that are most common in the conventional chemical industry. Unit operations used in advanced or new process technologies are generally not available. While these packages present apparently user-friendly interfaces, a considerable amount of chemical engineering knowledge is required to use them.

A project in its initial stages of development often requires top-level systems analysis that includes performance treatment alternatives, cost, and risk studies. This early analysis is generally characterized by a rough order-of-magnitude type of study. This type of analysis is particularly useful when the system includes innovative technologies when limited experimental data are available to develop a full thermodynamic model. The commercial packages require a substantial investment for analysis of technologies when little information is available. Consequently, a different type of simulation is required at the early stages of development. FLOW was designed to fill this need.

FLOW's name was derived from the fact that FLOW creates and analyzes flowsheets. The FLOW package includes several features that make it useful for flowsheet application:

- easy access to unit operations,
- simplified procedure for data input,
- straightforward execution of the simulation, and
- simple procedure to change and rerun the problem.

The package also allows the user to add new unit operations, if required. Other useful features of FLOW are described in Appendix E.

### **5.1.2 Use of FLOW in Systems Analysis**

FLOW has been used in support of the Oak Ridge FFCA and MWTF activities as a global systems analysis tool. The global systems analysis considered that mixed waste streams may be treated with several existing or potential treatment alternatives. Analysis of different scenarios is a mandatory activity specially when decisions on future process implementation are going to be made that have to conform with restrictions. FLOW has served as the central tool for this type of analysis by delivering information about cost, risk, and performance for the different scenarios. This information has typically been compiled within the context of several selection criteria from which a ranked list of alternatives is the final product of the analysis methodology. These analyses have greatly aided the management decision process.

FLOW has also been used to perform life-cycle cost estimation for the K-31 decontamination and decommission (D&D) activities. In all of these examples, FLOW has demonstrated robustness and flexibility as an analysis tool. Analysis of the performance of one specific process such as GMODS is a natural use of the FLOW capabilities.

## **5.2 GMODS FLOW MODEL ASSUMPTIONS AND OVERVIEW**

This subsection describes some of the general assumptions used to translate the GMODS process description into a FLOW process model. An overview of the model is also given.

In the spirit of the admonishment, "The map is not the territory," we remind that a FLOW model is not the GMODS process. The purpose of a simulation is to shape the design and implementation of the process. This simulation is intended to look at the time-averaged material flows, compositions, conformance to specifications, and product quality of GMODS for a variety of plant feed materials. A number of simplifications and assumptions are incorporated into the model that do not mirror the GMODS process exactly. But these simplifications and assumptions are made so that the essential behavior of GMODS with respect to the purpose of the study is captured while facilitating the calculations. Some of the more important assumptions are as follows:

**Steady-state.** GMODS is a multistep, batch, dynamic process. FLOW treats it as a steady-state, continuous process. Because we are interested in time-averaged flows from the process rather than instantaneous conditions, this is a good approximation. A dynamic simulation would have only complicated reaching the objectives of the simulation.

**Single process vessel.** Most of the various steps of the GMODS process are described as taking place in a single vessel in an induction furnace. The FLOW model of GMODS sequences through a FLOWsheet of unit operations connected by streams. In a continuous process, the unit operations are considered distinct equipment items connected by pipes. For this simulation, the FLOW unit operation models can be thought of as processes steps taking place in the same vessel, and the connecting streams can be considered the materials added or removed from that vessel at different times. Again, because we are not interested (for this study) in the time and space behavior inside the vessel, this is a reasonable assumption.

**Phase equilibria.** Solubilities and distribution of constituents between phases are estimated based on experimental data and then entered by the analyst, approximated by FLOW by its group or phase separator modules, or assumed based on engineering judgement. FLOW does not include rigorous thermodynamic models. Although the absence of this capability can be a problem for detailed design, FLOW's approximate methods are beneficial for preliminary analysis. Rigorous simulators typically spend 80% of execution time on thermodynamic calculations, and when the thermodynamics of the system is not well understood, one must be suspicious of the results of such calculations.

**Chemical kinetics and equilibrium.** Reaction equilibria are assigned by the analyst, and the residence-time in the vessel is assumed to be long enough to achieve an assumed extent of reaction. In a FLOW chemical reactor, the user specifies a relative kinetic constant and extent. The relative kinetic constant is used to sequence a series of reactions, not to size the reaction vessel.

Assumptions related to specific models are described in the following:

- The block diagrams in Fig. 5.1 compares the steps of the GMODS process with the sequence of operations in the GMODS FLOW simulation. In the left column, each box indicates a major GMODS process steps. In the right column, a box enclosed by a single line indicates a FLOW unit operation module, and a box enclosed by a double line indicates an entire FLOWsheet, either top-level or subsidiary level. Whereas the GMODS process description starts with the melter filled with an excess of lead-borate glass and lead metal, the FLOW model adds the lead-borate glass to the melter based on the waste quantity and composition. One step added in the FLOW model is an estimation of the plutonium concentration in the final glass product. This step is added to be sure that the product will satisfy criticality limits. Oxidation, dissolution, and glass

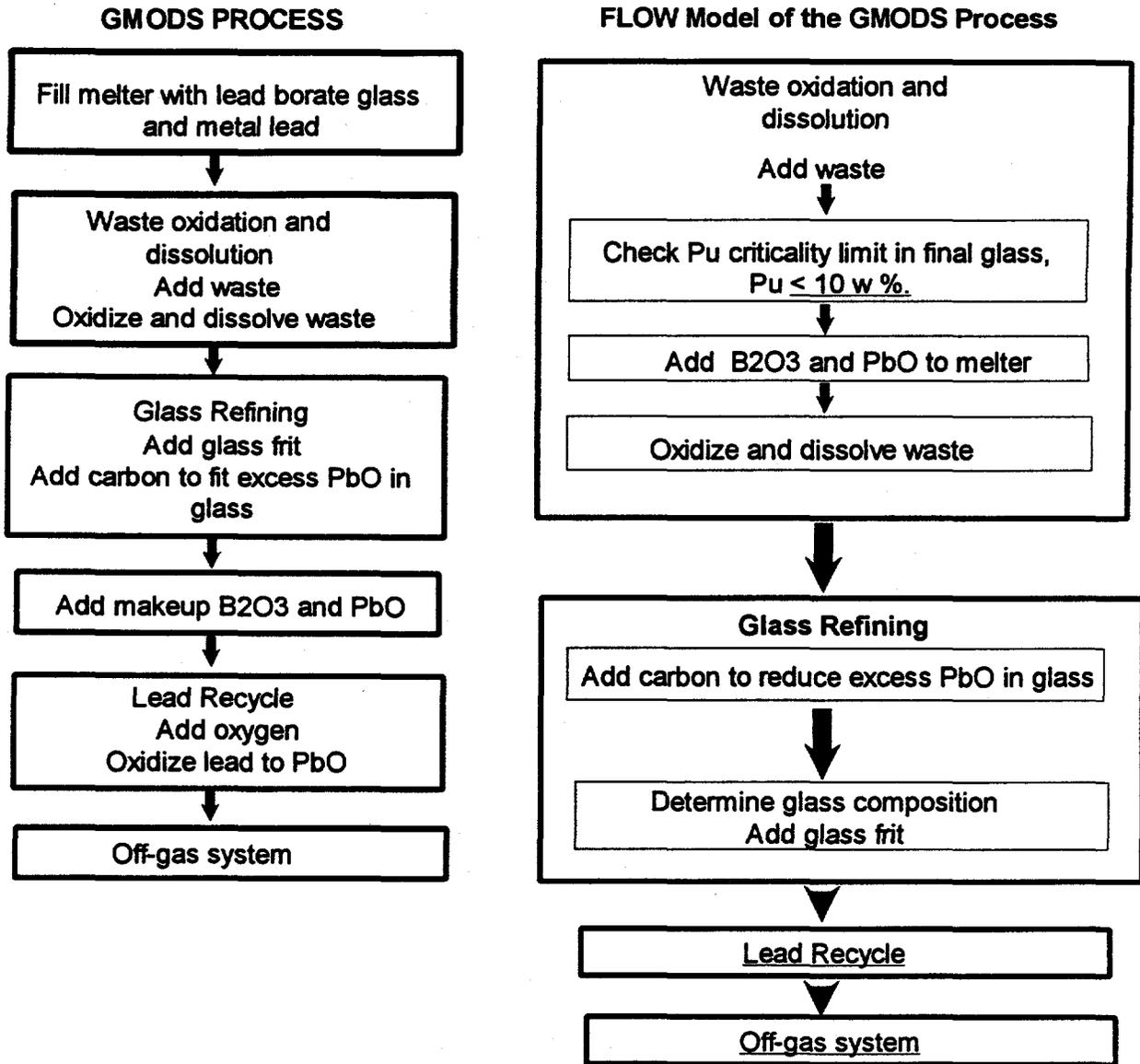


Fig. 5.1 Correspondence between GMODS and FLOW.

refining are combined in one FLOW aggregate FLOWsheet for these GMODS steps. The lead recycle and off-gas systems are contained in separate sub-FLOWsheets.

- Figure 5.2 presents the top-level GMODS model FLOWsheet. Both lower-level ("aggregate") FLOWsheets and FLOW process modules are represented on the FLOWsheet by icons. The streams connecting these processes are represented by lines. The aggregate flowsheets shown in Fig. 5.2 that are visible at the top level are labeled Pu\_Feed, CHECKPU, PBO\_B\_VA, NaOH\_Scrub\_Offgas, RXNSIADD, and Pb\_Oxid.

Referring to Fig. 5.2, Pu\_Feed blends the wastes and feeds the composite stream to the FLOWsheet. CHECKPU looks ahead to see if the final glass product will contain too much plutonium and terminates the simulation if the limit is exceeded. High concentrations of plutonium in the glass may

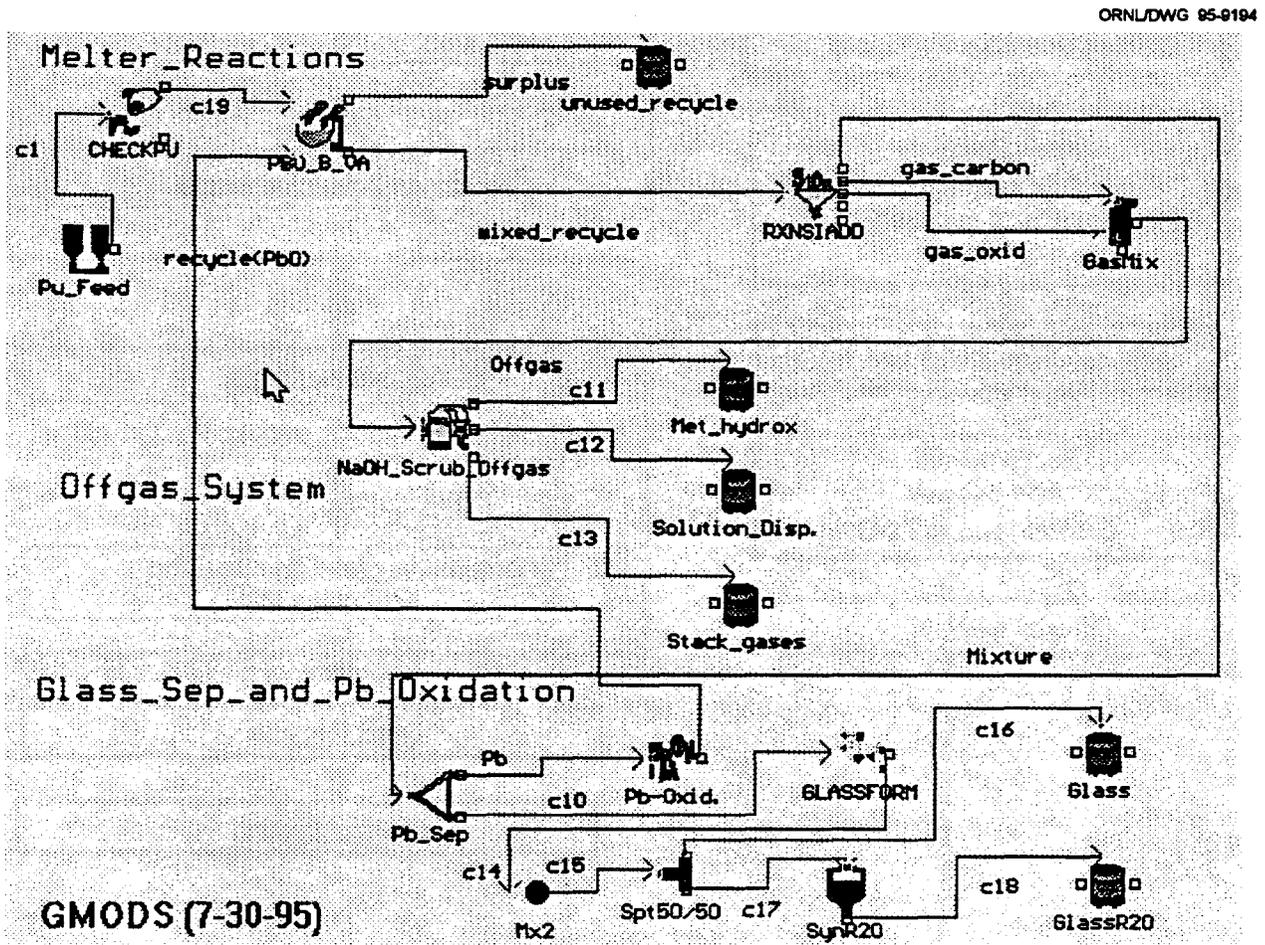


Fig. 5.2 Top-level GMODS FLOWsheet.

cause nuclear criticality, PBO\_B\_VA adds PbO and B<sub>2</sub>O<sub>3</sub>, and RXNSIADD (reactions and silicon addition) oxidizes the waste metals and organics and calculates how much silicon dioxide (SiO<sub>2</sub>) must be added to form the desired glass. Two off-gas streams and a glass-lead metal stream exit from this FLOWsheet.

The off-gas streams arise from the oxidation reactions and from the reaction with carbon. The off-gas streams are combined in a mixer and sent to the gas treatment system, NaOH\_Scrub\_Offgas. The glass and lead are separated in a component separator (Pb\_Sep), corresponding to the density separation of the lead and glass in the reactor vessel. The lead stream goes to Pb-Oxid (lead oxidation), which oxidizes the lead metal back to PbO and is recycled back to the lead oxide addition module. The glass stream is sent to a drum to terminate the FLOWsheet. Information is also obtained from the glass stream in synR<sub>2</sub>O, which determines the quantity of oxides that are used in the tertiary phase diagram glass calculations. This is done by taking an information stream using a multiplier, a splitter and a synonym, which converts any of the oxides in the glass except PbO and B<sub>2</sub>O<sub>3</sub> to R<sub>2</sub>O (oxides can be CaO, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, etc).

As mentioned previously, a difference between the GMODS process and the FLOW model is that GMODS starts with a vessel filled with a lead-borate glass and lead metal, whereas the FLOW model first calculates the amount of PbO and B<sub>2</sub>O<sub>3</sub> to add based on the waste characteristics. A second difference is the CHECKPU module, which looks ahead to see if it will be worthwhile to complete the FLOWsheet simulation.

In Sect. 5.4, each aggregate FLOWsheet is discussed. However, before getting into the FLOWsheet details, we will discuss several of the FLOW modules developed for this study that have been incorporated into the sub-FLOWsheets.

### 5.3 NEW FLOW MODULES DEVELOPED FOR THIS STUDY

Several new FLOW process modules were developed for this study. By *module* we mean a unit operation model or a FLOWsheet tool with its own executable code. Modules are represented by icons. FLOW models of unit operations and of entire plants can also be constructed from existing modules and from other FLOWsheets.

The following five modules were developed for this study:

**StreamFile** reads user supplied stream data from a file. This is useful for inputting waste streams, makeup streams, etc.

**CheckLimit**, a process used by the CHECKPU module, predicts the weight fraction of plutonium in the glass product. If the user-specified limit is exceeded, the module's output stream is zero. This is to address criticality concerns by keeping the Pu below a certain limit.

**Lim\_Cond** is the companion module to (Check\_Pu-limit). It compares the waste stream composition with the output from (Check\_Pu-limit). If the limit is exceeded, the simulation is stopped. This is to address criticality concerns by keeping the Pu below a certain limit.

**CH\_FEED1** adds an amount of a user-specified compound to the stream based on how much of it is required in its reactions with other stream compounds. This is useful, for example, for determining how much oxygen must be added for complete oxidation. An excess amount can be also be added. This module is used frequently throughout the FLOWsheets.

**GlassForm** calculates the amount of  $\text{SiO}_2$  that must be added to the melt to maximize the glass loading. A companion module (still being developed) brings the melt viscosity into an acceptable range by adding other constituents and adjusting the temperature. This module works, as described in the following.

Calculation of the glass form module are based on the ternary phase diagram of lead-borate glass (see phase diagram in Sect. 4). The vertices of the ternary phase diagram, A, B, and C (A =  $\text{SiO}_2$ , B =  $\text{B}_2\text{O}_3$ , and C =  $\text{R}_2\text{O}$ —waste oxides, other additives, and PbO), represent 100% A or B or C. Beginning with a starting composition somewhere in the ternary phase diagram, a line is drawn from the starting point to the A and B vertices. Each type of glass can have a region of acceptable waste form performance. For borosilicate glass, this region of acceptable glass compositions with respect to waste form performance has an elliptical shape. For our purposes, we assumed that this acceptable region is a perfect ellipse and that the coordinates of this region is defined by entering four points, the intersections with the minor and major axes. These data for borosilicate glass are stored in a file (GLASS.DB in Appendix C). The algorithm searches for the point on the surface of the ellipse that results in the maximum waste loading in the glass. This corresponds to a line that is tangent to the elliptical region and perpendicular to the vertex C. The algorithm can handle cases in which the desired region is tangent to a phase-diagram edge or is cut by the nonglass-region line.

The FLOW module outputs the original waste composition and the glass formers required to produce the maximum-loaded glass. Parameters supplied by the user include the "minimum design temperature" of the melter; the Gibbs free energy of hydration, which is related to glass durability and to the release rates of silicon and boron (you want  $\Delta G \geq -7.5$  kcal/mol); and compound check, constraints on the maximum weight percent of four compounds (see file GLASS.CPD in Appendix C). Adjusting the  $\Delta G$  is more difficult than adjusting the viscosity, although the free energy rarely needs to be adjusted. When an adjustment is required, other components are added to the glass. Viscosity is calculated by the program as well.

A spreadsheet created by Carol Jantzen<sup>9</sup> (SRL) formed the basis for the list of compounds useful for adjusting the viscosity, the calculation of  $\Delta G$ , viscosity, and liquidus. We used a different method for arriving at the desired composition than Jantzen. The method of Jantzen does not account for oxides already in the waste.

## 5.4 GMODS FLOWSHEETS

This subsection describes the aggregate FLOWsheets that make up the GMODS model.

**Plutonium Feed** blends the desired waste feed for the simulation and consists of a sub-FLOWsheet and two sub-sub-FLOWsheets. The first-level flowsheet, FEED.FLW, has two secondary aggregate flowsheets that do the actual work of reading the waste compositions and blending. Figures 5.3a-5.3c show these FLOWsheets. The module Syn\_Table\_401 converts the components as read from the sub-FLOWsheets waste composition files and converts these to chemical formulas (according to the synonym files shown in Appendix C) that will be needed later in the FLOWsheet reactions. The second-level aggregate FLOWsheets are labeled Pu\_Feed1 and Pu\_Feed2. Because 12 different categories of wastes can be fed, the blending of these was divided into two parts to make the FLOWsheets a little cleaner. "Stream File" modules (e.g., labeled Pits, Clean\_Metal, Impure\_Metal) are used to read waste compositions from files (using "SRT" extension, e.g., filename.srt) specified by the user. The stream is then operated on to adjust the overall blend of wastes using a splitter. The user specifies the percent of each stream that is to be included in the feed and these streams are blended in a mixer.

The categories of materials included in this study include the following: Pits, Clean\_metal, Impure\_metal, Clean\_Oxide, Impure\_Oxide, Compounds, Rich\_Scrap, Reactor\_Fuel, Irradiated\_Fuel, Miscellaneous, and User\_Input.

The categories for the two substreams, RS and LS, included ash; ceramic crucibles; chloride salts; combustibles; firebrick; glass; graphite; grit blasting residues; heels; insulation; ion-exchange resins; leaded gloves; nonconforming; plutonium fluorides; sand, slag, and concrete (SS&C); scrap metal; sludges; and solutions.

**Check Plutonium in Glass Specification** predicts the plutonium content of the final glass product, and aborts the simulation if the Pu content is too high. Figure 5.4 shows the Check Plutonium FLOWsheet based on the user-specified permissible Pu content. The FLOWsheet duplicates some of the top-level FLOWsheet to arrive at the final product composition and to determine if this composition is acceptable with respect to criticality.

**Makeup PbO and B<sub>2</sub>O<sub>3</sub>** adds PbO and B<sub>2</sub>O<sub>3</sub> by calculating the PbO required to oxidize metals and organics and adding B<sub>2</sub>O<sub>3</sub> to arrive at the proper PbO:B<sub>2</sub>O<sub>3</sub> molar ratio. Figure 5.5 shows the Makeup FLOWsheet. Inputs to this module include the waste stream and the recycled PbO. The waste stream is multiplied and split. One branch of the split is used to calculate the PbO required to oxidize metals and the other branch is used to calculate the amount of PbO required to oxidize organics. In the aggregate, Rec/Feed\_Valve, the user specifies a reaction file; the component to be

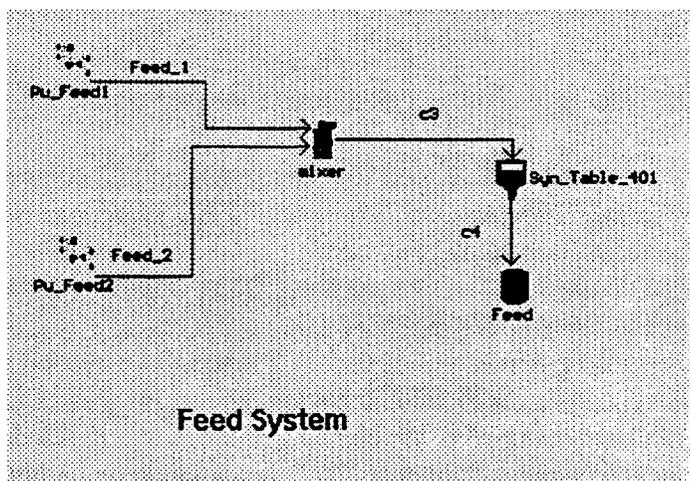


Fig. 5.3a. Feed blend aggregate FLOWsheets.

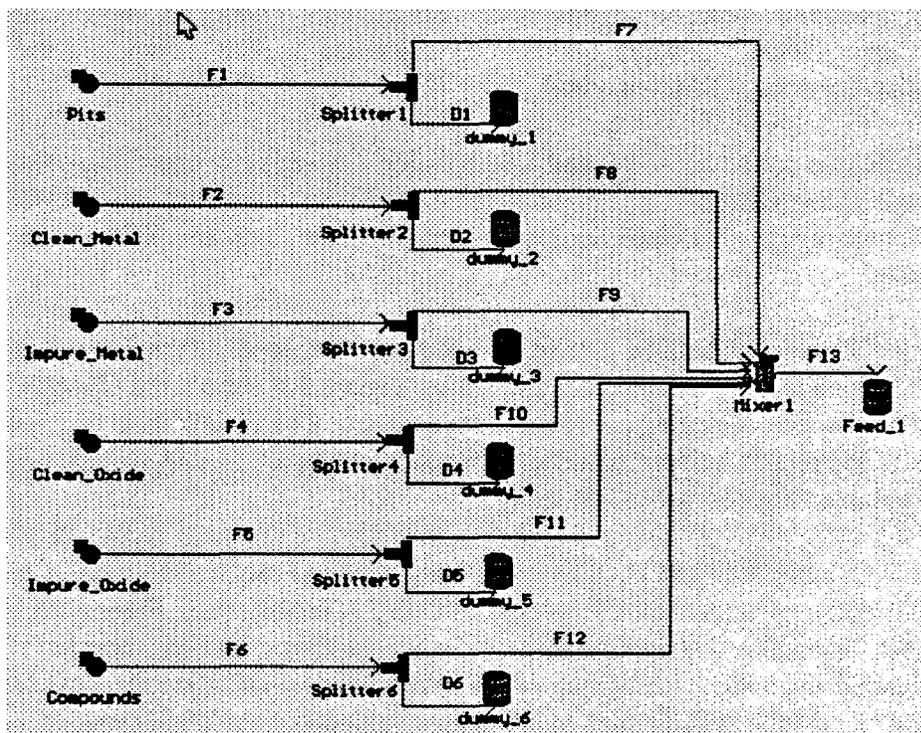


Fig. 5.3b. Aggregate FLOWsheet Pu\_Feed1.

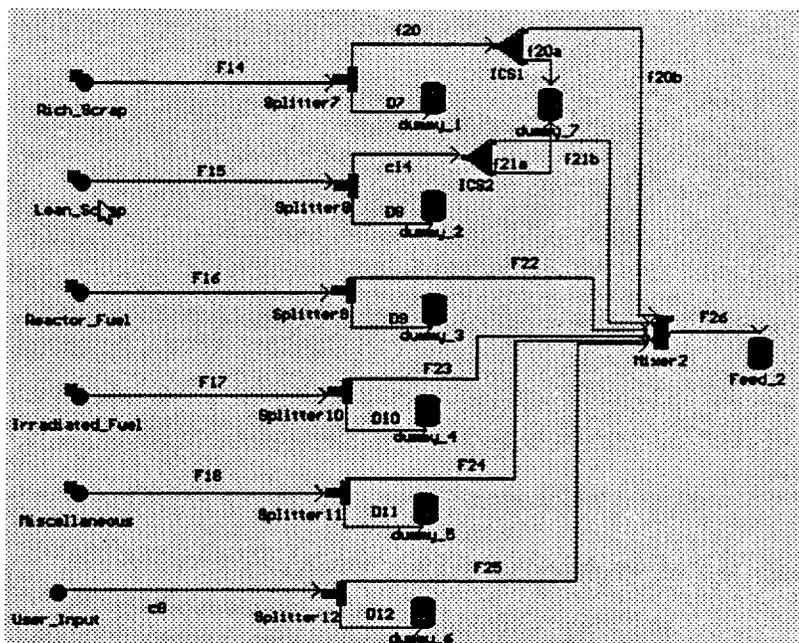


Fig. 5.3c. Aggregate FLOWsheet Pu\_Feed2.

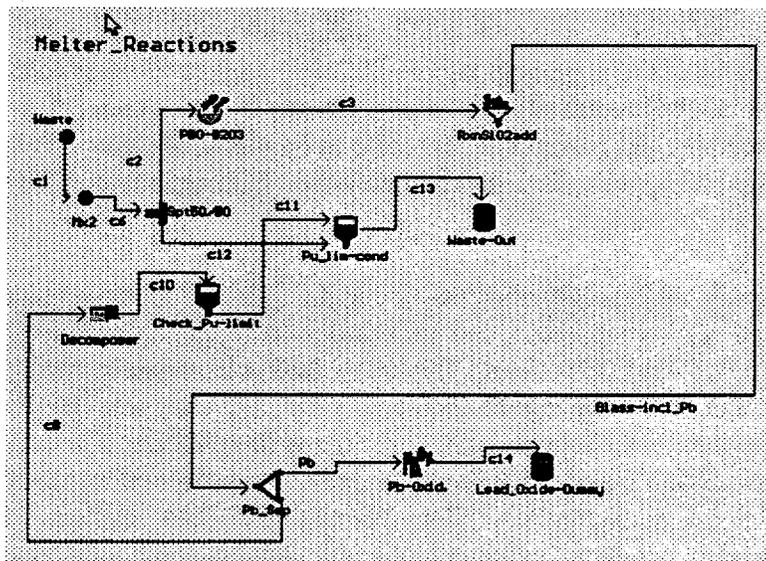


Fig. 5.4 CHECKPU FLOWsheet.

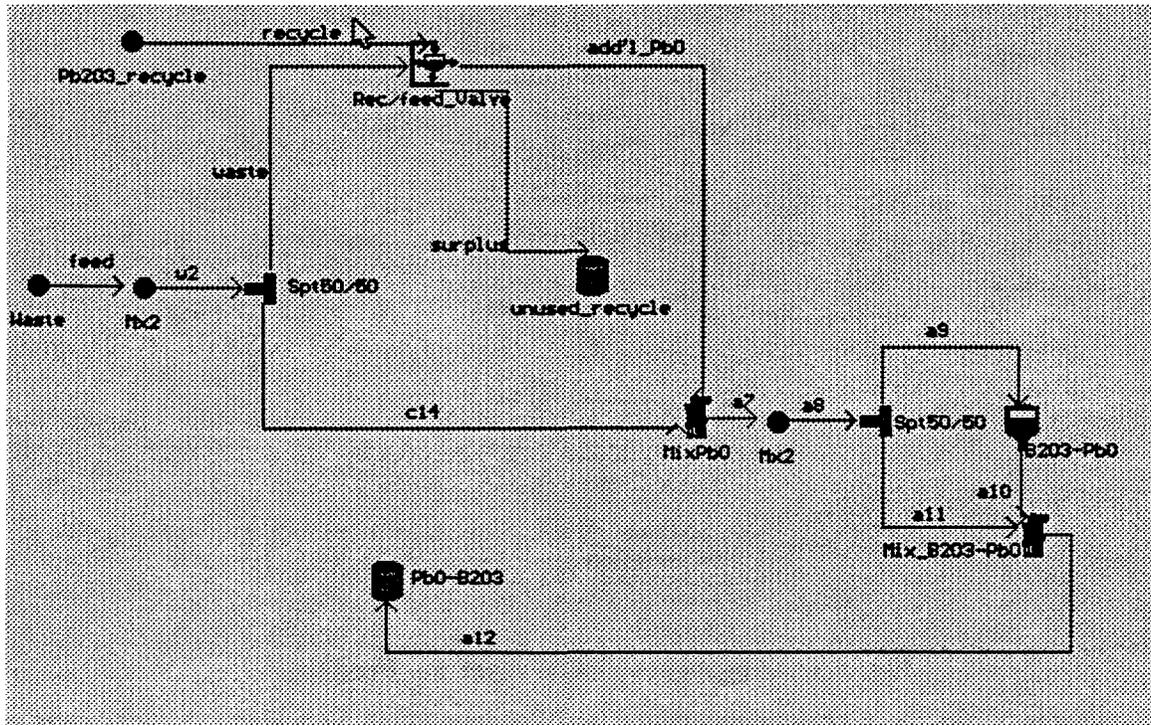


Fig. 5.5 Makeup PbO and B<sub>2</sub>O<sub>3</sub> FLOWsheet.

added, in this case PbO; and the percent excess PbO (set to 0 in these simulations). The module calculates the additional PbO required over what is already in the stream. A similar module, B<sub>2</sub>O<sub>3</sub>-PbO, adds B<sub>2</sub>O<sub>3</sub>. The PbO:B<sub>2</sub>O<sub>3</sub> molar ratio may have to be modified later if B<sub>2</sub>O<sub>3</sub> is too high or too low. This module uses a single-reaction reactor with a stoichiometric factor of B<sub>2</sub>O<sub>3</sub>:PbO of 1:10 to give the appropriate molar ratio.

**Oxidize and Dissolve Feed** reacts metals, halides, and organics waste feed components with PbO, adds SiO<sub>2</sub> to adjust the glass composition, and adds carbon to remove excess PbO. Figure 5.6 shows the Oxidize and Dissolve Feed FLOWsheet. The waste feed is first passed through a heat exchanger (Induction) to raise the feed temperature above melting. The user sets the glass melter operating temperature at the top-level FLOWsheet, 1050°C for these simulations. The reactor Waste Ox-PbO is where all waste oxidation reactions take place, and the corresponding reactions in reaction-file PbO-Oxid.rxn are listed in Table 5.1. The reaction file lists reactants, molecular weights, stoichiometric coefficients, products, product molecular weights and coefficients, extent of reaction and a reaction ordering parameter. The reaction list will grow larger as more is known about the waste stream composition. Each line in Table 5.1 represents a reaction. The first two elements are

reactants, the next two elements are the respective molecular weights for the reactants, the next two elements are the respective stoichiometric coefficients, the next four elements are the products, the next four elements are the respective molecular weights of the products, the next four elements are the stoichiometric coefficients of the product, and the last two elements of the line are the conversion and the kinetic parameter, respectively. In case of reactions in series in which the same reactants are

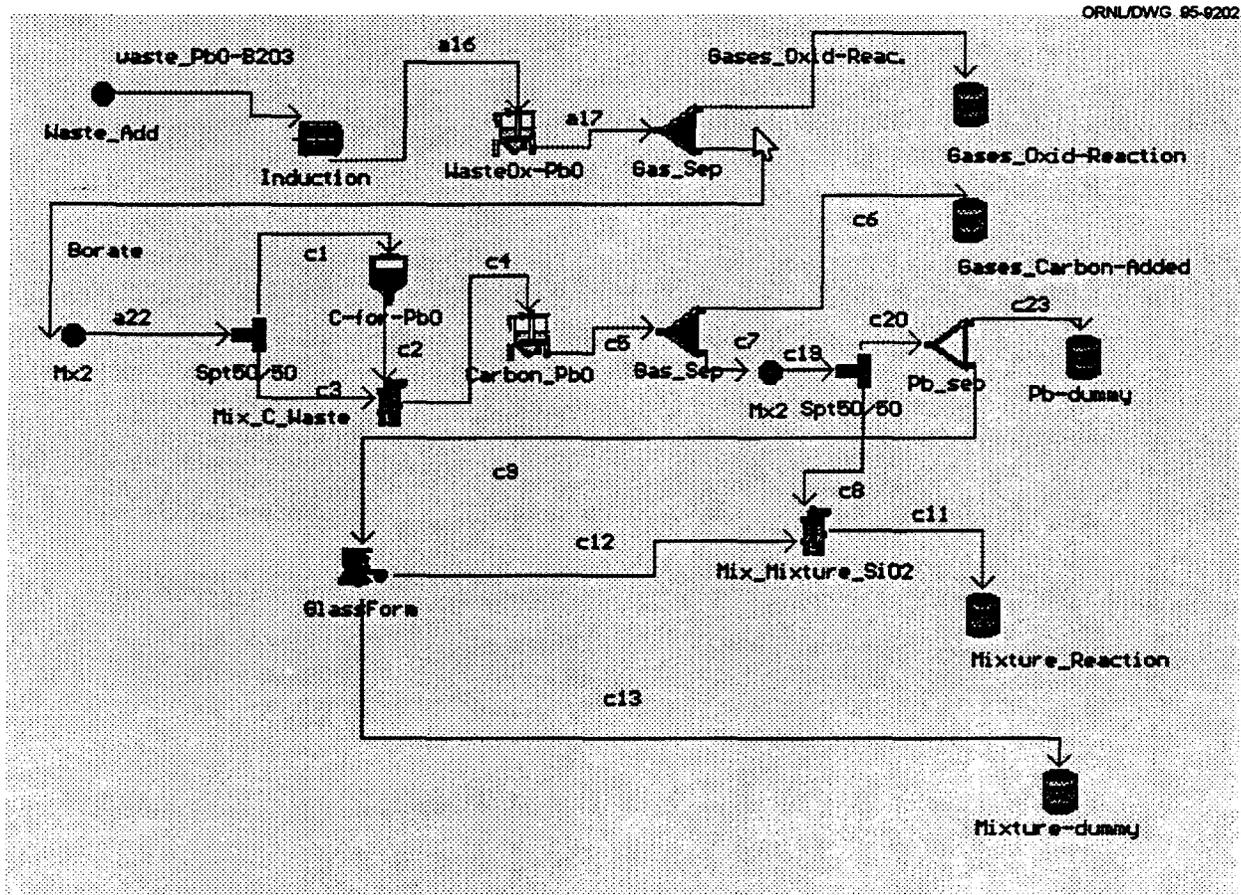


Fig. 5.6 Oxidize and dissolve feed.

involved, the reaction that will be performed first is the one that has the highest kinetic coefficient; if reactants are left the reaction that has the second largest kinetic coefficient will follow.

The reactor can model parallel or series reactions. The products from the reactor are separated into a gas and liquid stream by a phase separator, Gas\_Sep. All gases are assumed to report to the gas stream which connects to the off-gas treatment system on the top-level FLOWsheet.

Table S.1 Reaction file PbO-oxid.rxn

R <sub>i</sub>	R <sub>j</sub>	MR <sub>i</sub>	MR <sub>j</sub>	SR <sub>i</sub>	SR <sub>j</sub>	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	P <sub>4</sub>	MP <sub>1</sub>	MP <sub>2</sub>	MP <sub>3</sub>	MP <sub>4</sub>	SP <sub>1</sub>	SP <sub>2</sub>	SP <sub>3</sub>	SP <sub>4</sub>	Extent	K <sub>kinetic</sub>
Pu	PbO	242	223.2	1	2.0	PbO <sub>2</sub>	Pb	-	-	74	207.2	0	0	1	2	0	0	0.999	99
Zr	PbO	91.22	223.2	1	2.0	ZrO <sub>2</sub>	Pb	-	-	123.22	207.2	0	0	1	2	0	0	1.0	98
Al	PbO	26.98	223.2	2	3.0	Al <sub>2</sub> O <sub>3</sub>	Pb	-	-	101.96	207.2	0	0	1	3	0	0	0.99	97
Fe	PbO	55.85	223.2	3	4.0	Fe <sub>2</sub> O <sub>3</sub>	Pb	-	-	231.55	207.2	0	0	1	4	0	0	0.99	96
CaCl <sub>2</sub>	PbO	110.98	223.2	1	1.0	PbCl <sub>2</sub>	CaO	-	-	278.1	56.08	44	0	1	1	0	0	0.999	95
CaCO <sub>3</sub>	-	100.08	0	1	0.0	CaO	CO <sub>2</sub>	-	-	56.08	44.0	0	0	1	1	0	0	1.00	99
Na <sub>2</sub> CO <sub>3</sub>	-	106	0	1	0.0	Na <sub>2</sub> O	CO <sub>2</sub>	-	-	62	44.0	0	0	1	1	0	0	1.00	99
CH <sub>3</sub> C <sub>2</sub> H <sub>4</sub> NH <sub>2</sub>	PbO	107	223.2	1	20.5	CO <sub>2</sub>	H <sub>2</sub> O	NO <sub>2</sub>	Pb	44	18.0	46	207.2	7	4.5	1	20.5	1.0	99
NaCl	PbO	58.45	223.2	2	1.0	Na <sub>2</sub> O	PbCl <sub>2</sub>	-	-	62	278.1	0	0	1	1	0	0	0.999	99
MgCl <sub>2</sub>	PbO	95.2	223.2	1	1.0	MgO	PbCl <sub>2</sub>	-	-	40.3	278.1	0	0	1	1	0	0	0.999	99
Kd	PbO	74.55	223.2	2	1.0	K <sub>2</sub> O	PbCl <sub>2</sub>	-	-	94.2	278.1	0	0	1	1	0	0	0.99999	99
PuF <sub>2</sub>	PbO	318	223.2	1	2.0	PbO <sub>2</sub>	PbF <sub>2</sub>	-	-	274	245.2	0	0	1	2	0	0	0.9999	99
CaF <sub>2</sub>	PbO	78.08	223.2	1	1.0	CaO	PbF <sub>2</sub>	-	-	56.08	245.20	0	0	1	1	0	0	0.9999	99
Mg	PbO	24.3	223.2	1	1.0	MgO	Pb	-	-	40.3	207.2	0	0	1	1	0	0	0.99	99
Ca	PbO	40.08	223.2	1	1.0	CaO	Pb	-	-	56.08	207.2	0	0	1	1	0	0	0.9999	99
HNO <sub>3</sub>	-	63	0	4	0.0	H <sub>2</sub> O	NO <sub>2</sub>	O <sub>2</sub>	-	18	46.0	32	0	2	4	1	0	0.999	99
C <sub>2</sub> H <sub>7</sub> O	PbO	59	223.2	2	17.0	CO <sub>2</sub>	H <sub>2</sub> O	Pb	-	44	18.0	207.2	0	6	7	17	0	0.999	99
C <sub>2</sub> H <sub>8</sub>	PbO	44	223.2	1	10.0	CO <sub>2</sub>	H <sub>2</sub> O	Pb	-	44	18.0	207.2	0	3	4	10	0	0.999	99
CH <sub>4</sub>	PbO	16	223.2	1	4.0	CO <sub>2</sub>	H <sub>2</sub> O	Pb	-	44	18.0	207.2	0	1	2	4	0	0.999	99
C <sub>2</sub> H <sub>2</sub> Cl	PbO	112.45	223.2	2	29.9	CO <sub>2</sub>	H <sub>2</sub> O	Cl <sub>2</sub>	Pb	44	1.08	70.9	207.2	12	5	1	29	0.999	99

R<sub>i</sub>, R<sub>j</sub> Reactants 1 and 2  
 MR<sub>i</sub>, MR<sub>j</sub> Mol-weight of R<sub>i</sub> and R<sub>j</sub>  
 SR<sub>i</sub>, SR<sub>j</sub> Stoich coefficient of R<sub>i</sub> and R<sub>j</sub>  
 P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, P<sub>4</sub> Products 1, 2, 3, and 4  
 MP<sub>1</sub>, MP<sub>2</sub>, MP<sub>3</sub>, MP<sub>4</sub> Mol-weight of products 1, 2, 3, and 4  
 SP<sub>1</sub>, SP<sub>2</sub>, SP<sub>3</sub>, SP<sub>4</sub> Stoich coefficient of products 1, 2, 3, and 4  
 Extent Extent of the reaction  
 K<sub>kinetic</sub> Kinetic parameters

The liquid stream is checked to determine how much carbon is needed to reduce the PbO using a multiplier, splitter, and a CH\_FEED1 labeled C-for-PbO. This is followed by reaction of the carbon with PbO in the series reactor, Carbon\_PbO (C\_PbO.RXN in Appendix C). The gases generated by this reaction are separated within a phase separator and routed to the off-gas system. The lead and glass stream are multiplied, split, and sent through a Pb separator to provide an information stream to the glass formulation module. The glass formulation module calculates the quantity of additives required, as described in Sect. 5.3. The GlassForm module has several parameters; GlassComponent1, GlassComponent2, GlassComponent3, and MinDesignTemperature. For this study, these were set at SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, R<sub>2</sub>O (i.e., borosilicate glass), and 1050°C, respectively. These additives are mixed with the glass stream. Chlorides are also eliminated in this step. They react with PbO to form lead chloride (PbCl<sub>2</sub>) + oxide. PbCl<sub>2</sub> volatilization is assumed. Gasses are separated, and the temperature is increased to the desired furnace temperature.

**Off-gas Treatment** removes volatile metal halides in a caustic scrubber. Figure 5.7 shows the off-gas treatment FLOWsheet. An information stream is input to NaOH\_req, which calculates the amount of NaOH required in the scrubber. Gasses are scrubbed in a reactor (NaOH\_Cl.RXN in Appendix C) and cooled to simulate a venturi scrubber. The clean gasses are routed to the stack on the top-level FLOWsheet, and the scrubber bottoms are separated into metal hydroxides, and NaCl solution.

**Lead Reoxidation** oxidizes metallic Pb for reuse. This is accomplished on the top-level FLOWsheet in the reactor labeled, Pb-Oxid. The PbO is recycled to the PBO\_B\_VA aggregate FLOWsheet. Figure 5.8 illustrates the process.

**Glass Former** checks the viscosity of the glass formed and corrects it if it does not fall in the correct range. Figure 5.9 shows the glass former FLOWsheet. The glass stream first passes through a glass former to make sure it is in the proper range to form glass. The stream then goes through the GlassPass module in which it checks the viscosity of the glass. If the viscosity is not in the proper range, a viscosity-improving compound such as Na<sub>2</sub>O is added to the glass. Then more glass formers such as SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> are added to bring the glass back into the correct glass-forming range. Finally, the stream passes through one more glass former in which it checks to make sure that the glass formed is in the proper range.

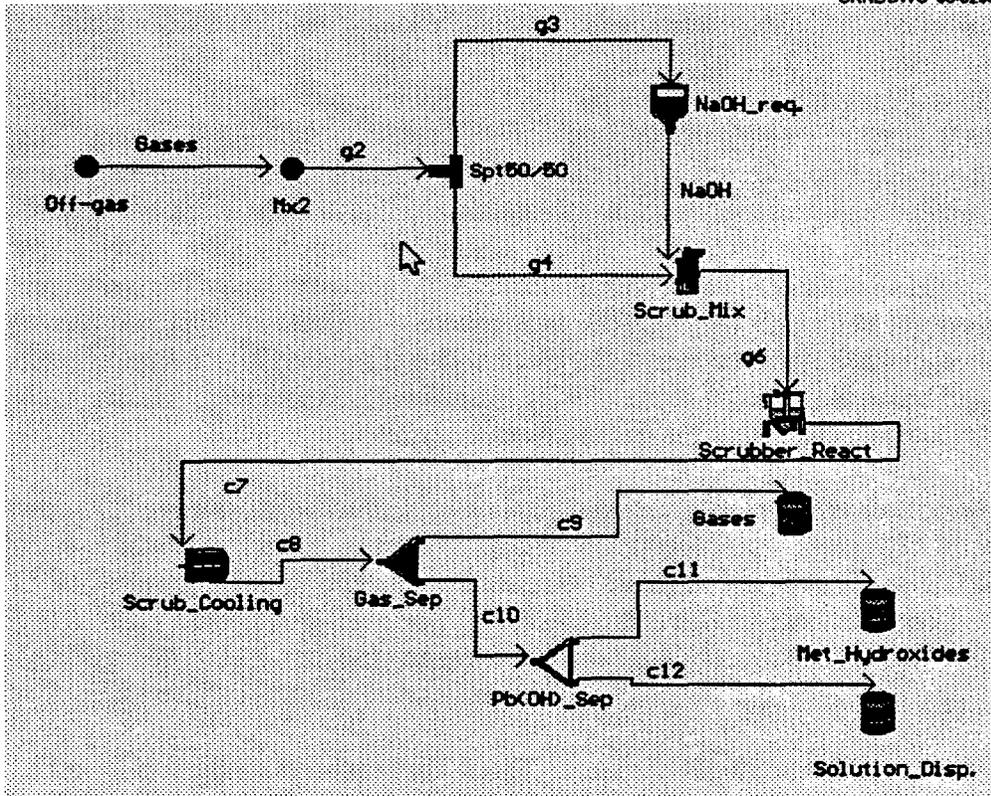


Fig. 5.7 Off-gas FLOWsheet.

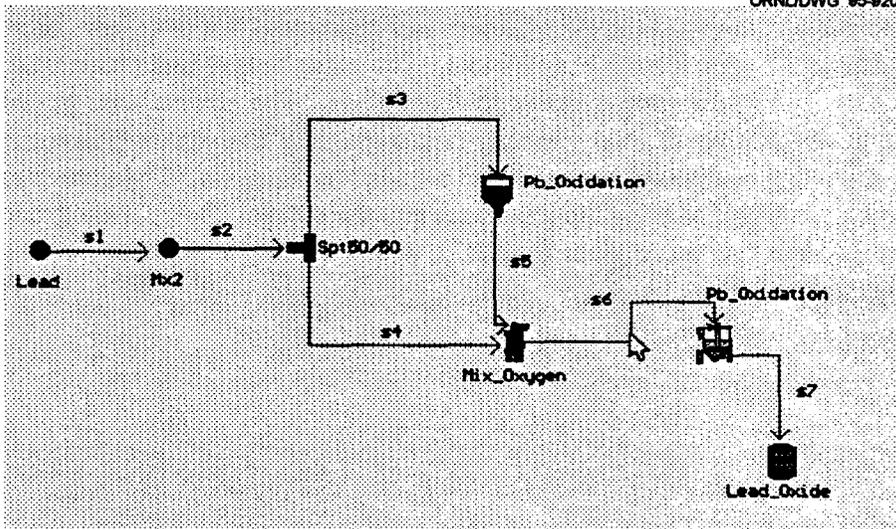


Fig. 5.8 Conversion of Pb into PbO.

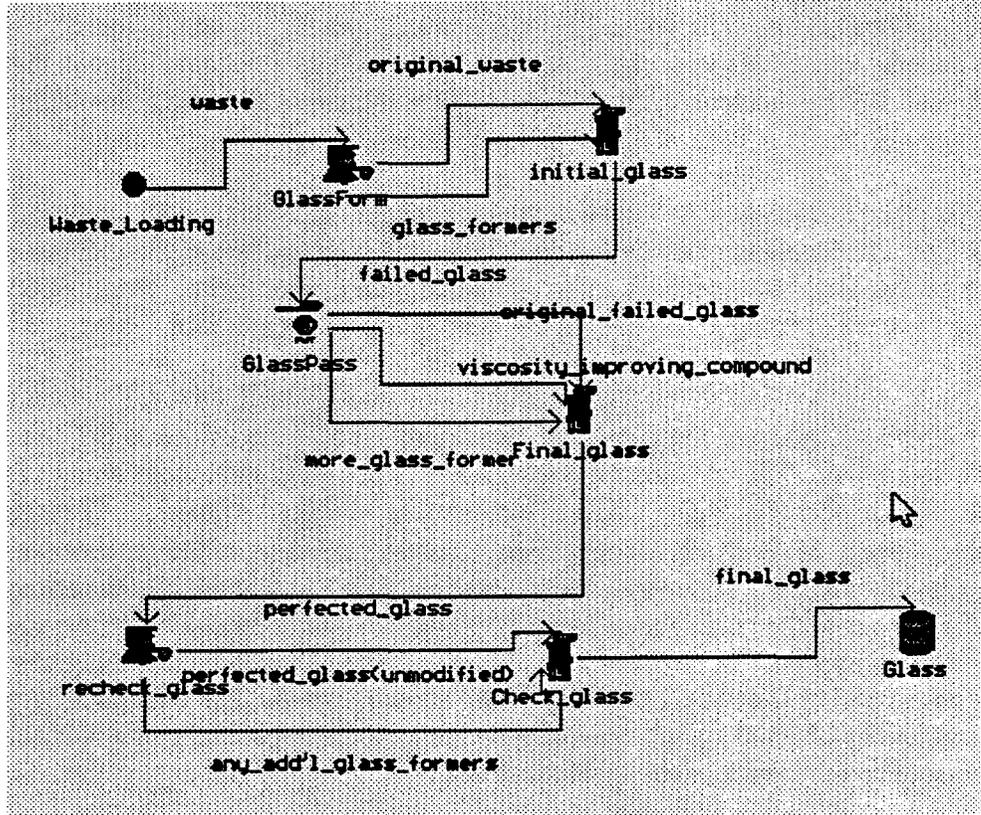


Fig. 5.9 Glass former aggregate FLOWsheet.

## 6. GMODS SIMULATION RESULTS

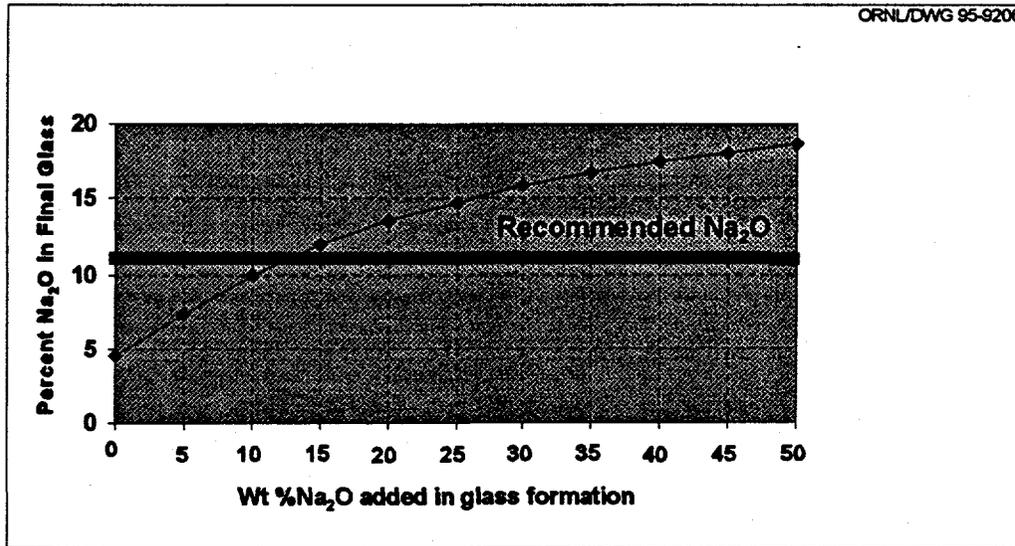
The GMODS process has been modeled using the simulator tool FLOW, which calculates the material flows of process streams by sequentially simulating the chemical and physical behavior of the process unit operations. The waste feed material selected for the simulation correspond to the RS and LS material located at the Rocky Flats site. Table A.1 in Appendix A shows the composition of the LS and RS by subcategories. Table C.2 in Appendix C shows the composition of each subcategory in the RS. Table C.3 shows the composition of each subcategory for the LS.<sup>1,2</sup>

GMODS can be used to treat all the waste streams at once or can be used to treat only specific waste categories. The blending of these various waste categories before treatment can often reduce the volume of the final glass because many waste contain one or more components of glass. Also, changing certain operating conditions of the GMODS process can lead to changes in the final glass volume.

What follows summarizes the results of simulation for RS, LS, blended RS and LS and an ash-chloride salt blend. The quantity of  $\text{Na}_2\text{O}$  added to the glass influences many of the variables of interest to the process designer.  $\text{Na}_2\text{O}$  is a component required to modify the viscosity and  $\Delta G$  of hydration. Several of the charts/tables present results as a function of the percentage of  $\text{Na}_2\text{O}$  added during glass formation. According to information from Savannah River experimental data,  $\text{Na}_2\text{O}$  should be present in the glass in approximately 10 wt %.<sup>3</sup> The composition of the glass that has been found to be appropriate in terms of stability, is extracted from a ternary diagram for borosilicate glasses developed at Clemson University<sup>12</sup> and shown Sect. 4. The final glass product is assumed to have a density of  $2800 \text{ kg/m}^3$ . Results also indicate the impact of producing glass by modifying the temperature of melting or the addition of  $\text{Na}_2\text{O}$ .

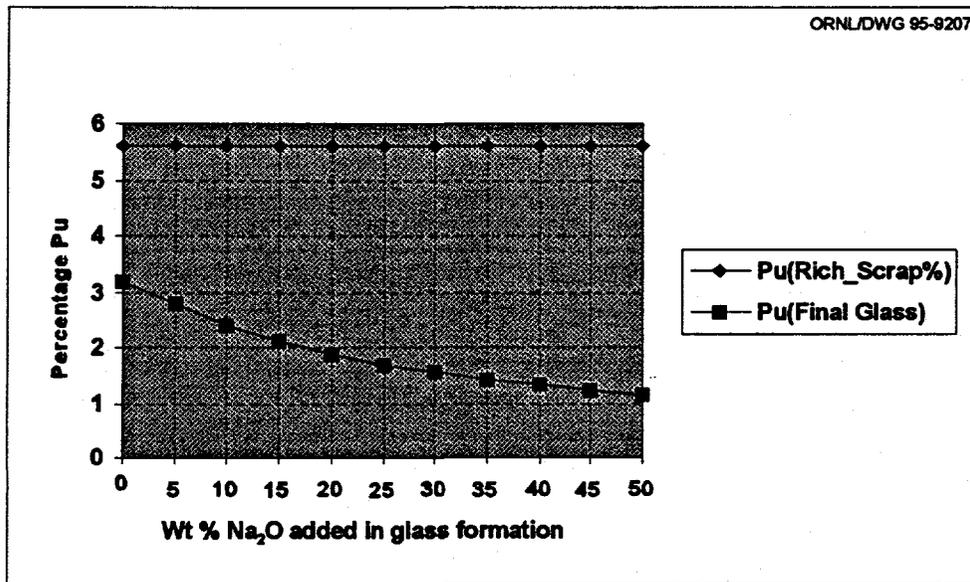
### 6.1 RESULTS OF TREATING ALL SUBCATEGORIES OF RS THROUGH THE GMODS PROCESS.

- The FLOW modeling process assumes that the  $\text{Na}_2\text{O}$  is added during the glass formation process (as shown in Sect. 5.4, Fig. 5.9). The percent of  $\text{Na}_2\text{O}$  added during the glass formation is based on the mass fed to the melter; consequently, the final  $\text{Na}_2\text{O}$  composition in the glass may not be the same as that added in the melter. According the experimental information from the SRL, a concentration of  $\text{Na}_2\text{O}$  of about 10 wt % is desirable in the final glass. For example, if every subcategory pertaining to RS were combined in one final waste, the addition of  $\text{Na}_2\text{O}$  and the resulting  $\text{Na}_2\text{O}$  concentrations in the final glass is illustrated in Fig. 6.1. To obtain a 10 wt % of  $\text{Na}_2\text{O}$  in the final glass, 10 wt %  $\text{Na}_2\text{O}$  (based on the melter feed) should be added during the glass formation process. The general assumption of this subsection is that every subcategory of RS has been combined into one waste stream.



**Fig. 6.1. Na<sub>2</sub>O composition in final glass vs weight percent added during the melting process for RS.**

- The content of Pu in the initial RS is about 5.7 wt %. Once treated by the GMODS process, the content of Pu in the final glass is approximately 2.4 wt % (see Fig. 6.2).



**Fig. 6.2. Percentage of Pu in initial RS and final glass.**

- At 10 wt % of  $\text{Na}_2\text{O}$ , the initial mass of RS was approximately 43,000 kg, resulting in approximately 95,000 kg ( $34 \text{ m}^3$ ) of final glass. The ratio of glass weight to waste is approximately 2.2 (Fig. 6.3).

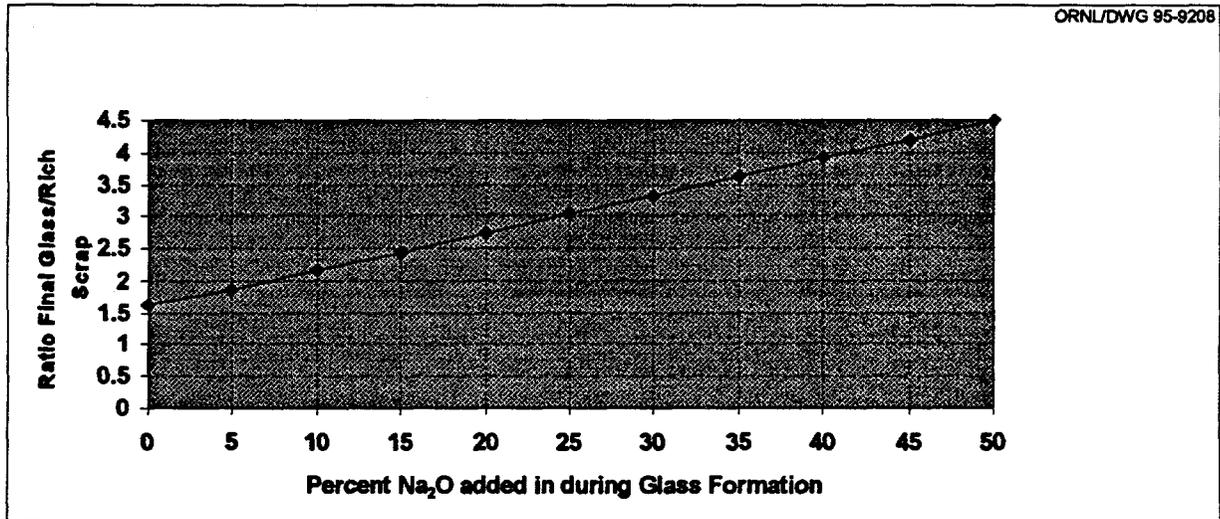


Fig. 6.3. Ratio of final glass:to initial RS mass.

- The  $\text{SiO}_2$  added to the glass formation is about 1.1, expressed as the ratio of  $\text{SiO}_2$  added to feed of RS (Fig. 6.4)

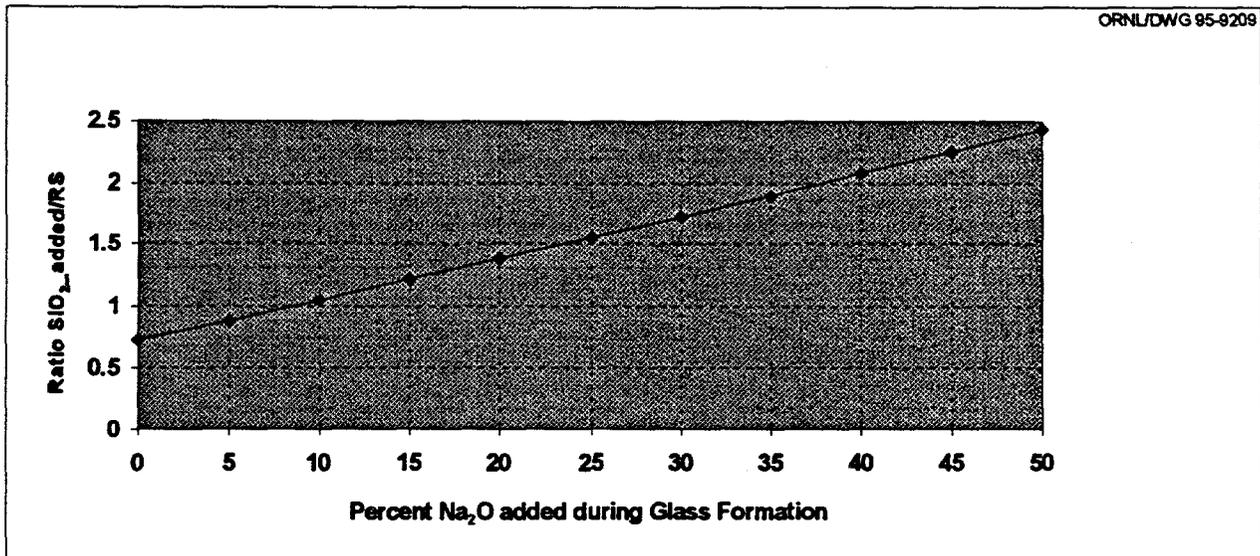


Fig. 6.4. Ratio of  $\text{SiO}_2$  to RS during for glass formation.

- The  $B_2O_3$  added to the glass formation is approximately 0.3, expressed as the ratio of  $B_2O_3$  to feed of RS (Fig. 6.5).

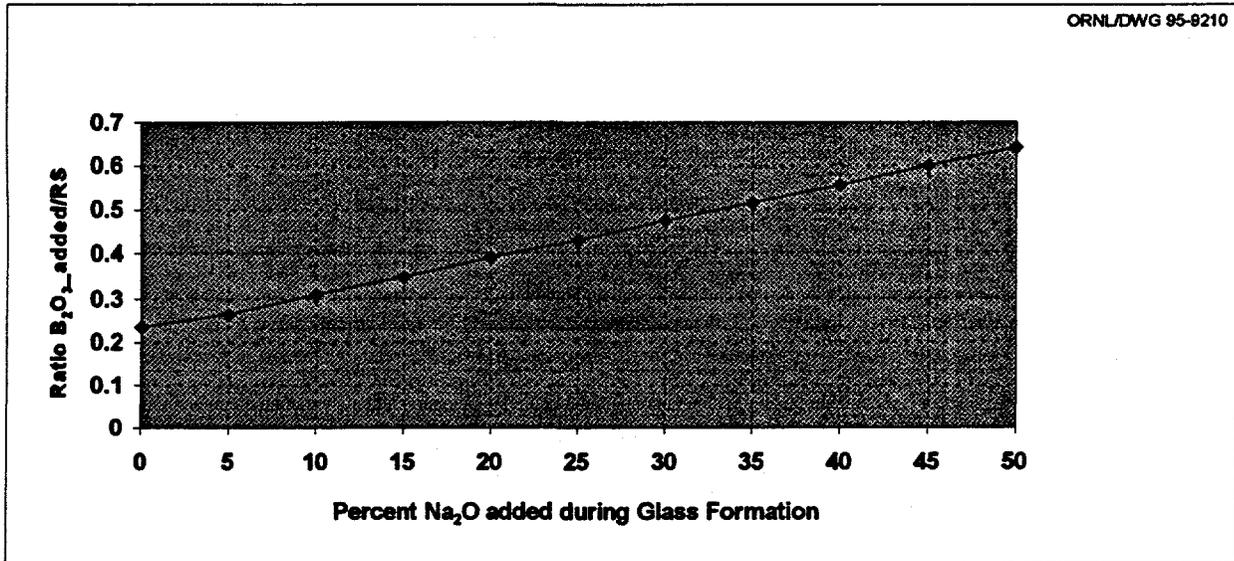


Fig. 6.5. Ratio of  $B_2O_3$  to RS added during the glass formation process.

- The melting temperature was set at approximately  $1175^\circ C$ . Increasing the amount of  $Na_2O$  would have reduced the melting temperature, but GMODS can operate safely at this temperature (Fig. 6.6).

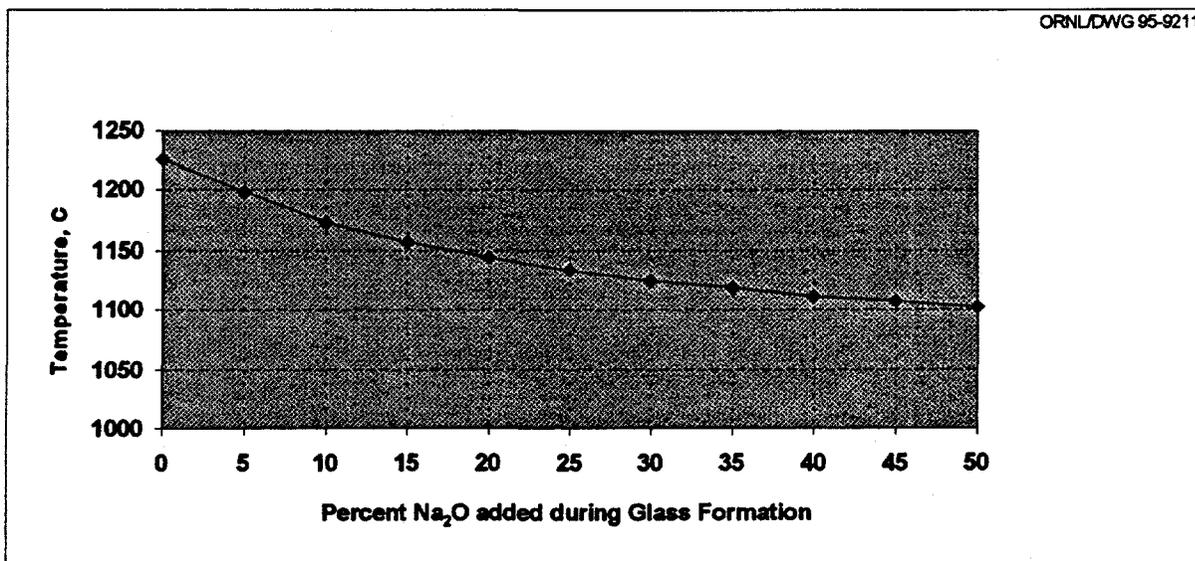


Fig. 6.6. Melting temperature vs  $Na_2O$  addition during the glass formation process.

## 6.2 RESULTS OF TREATING ALL SUBCATEGORIES OF LS WITH THE GMODS PROCESS.

- In order to obtain 10 wt % of  $\text{Na}_2\text{O}$  in the final glass, 15 wt %  $\text{Na}_2\text{O}$  (based on the feed) should be added during the glass formation (Fig. 6.7).

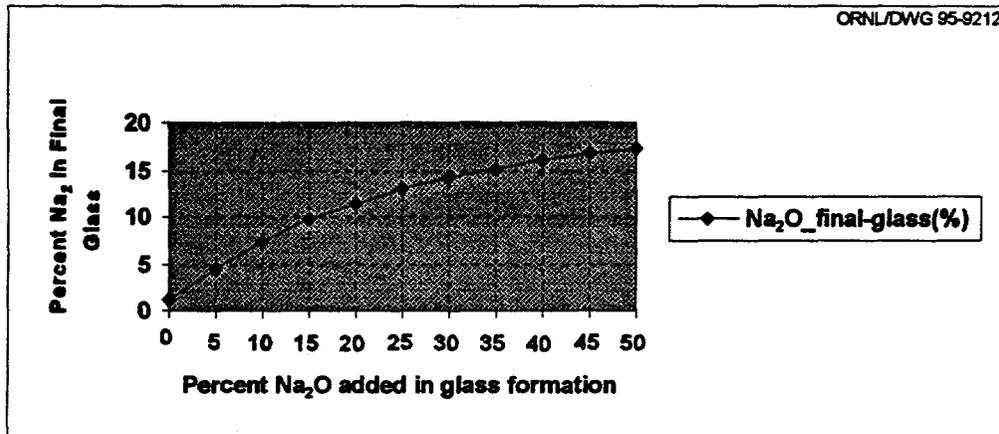


Fig. 6.7.  $\text{Na}_2\text{O}$  composition in final glass vs weight percent added during the melting process for LS.

- The content of Pu in the initial LS is approximately 0.19 wt %. Once treated by the GMODS process, the content of Pu in the final glass is approximately 0.06 wt % (Fig. 6.8).

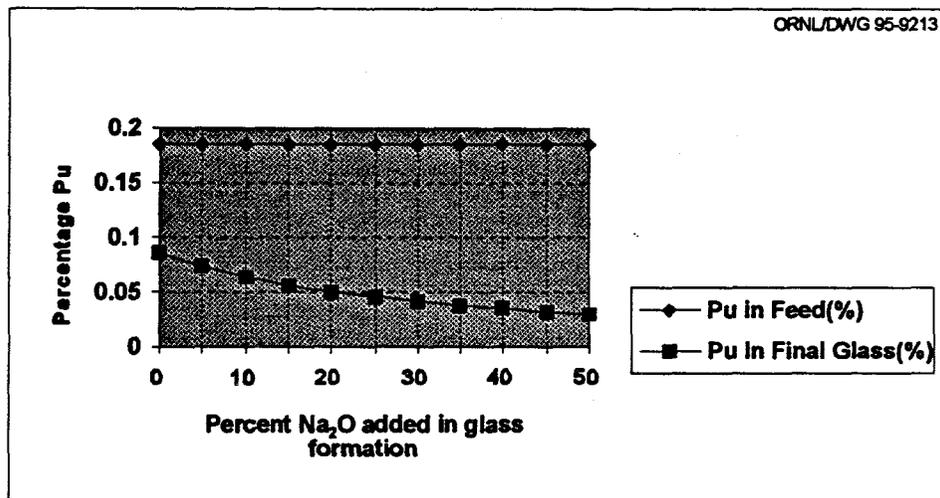


Fig. 6.8. Pu wt % in LS and final glass formation.

- The initial mass of LS was approximately 230,000 kg, resulting in approximately 650,000 kg (232 m<sup>3</sup>) of final glass. The ratio of glass to waste is about 2.8.
- The SiO<sub>2</sub> added to the glass formation is approximately 1.3, expressed as the ratio of SiO<sub>2</sub> added to feed of LS (Fig. 6.9).

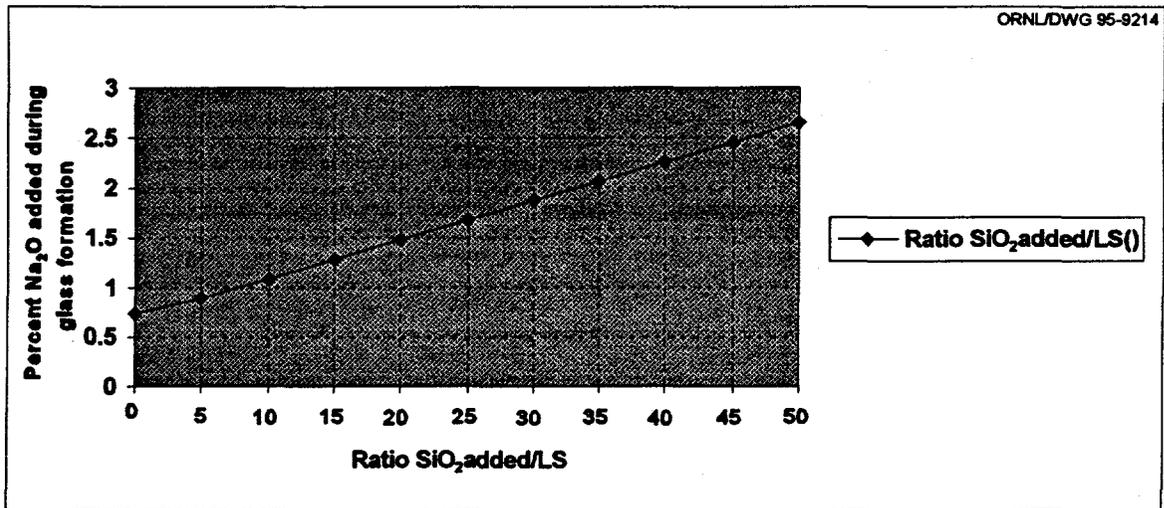


Fig. 6.9. Ratio of SiO<sub>2</sub> to LS added during the glass formation process.

- The B<sub>2</sub>O<sub>3</sub> added to the glass formation is about 0.5, expressed as the ratio of B<sub>2</sub>O<sub>3</sub> added to feed of LS (Fig. 6.10).

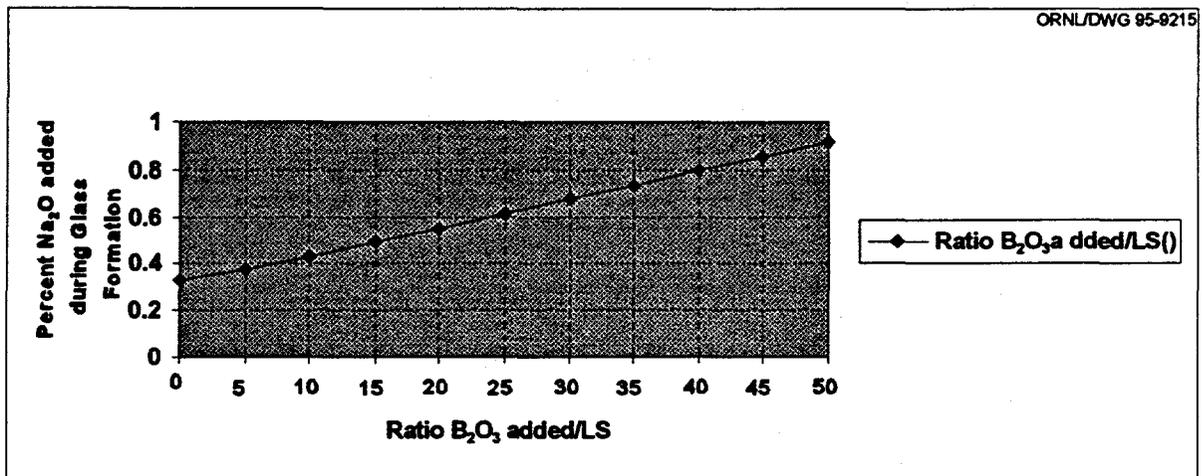


Fig. 6.10. Ratio of B<sub>2</sub>O<sub>3</sub> to LS added during the glass formation process.

- The melting temperature was set at about 1150°C. (Fig. 6.11).

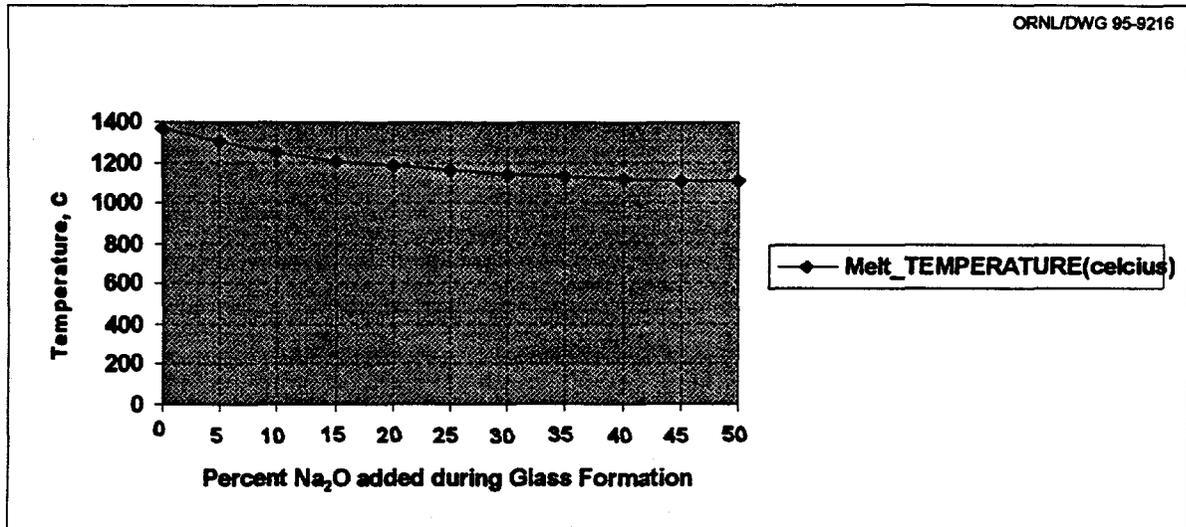


Fig. 6.11. Melting temperature vs Na<sub>2</sub>O added during the glass formation process.

### 6.3 RESULTS OF TREATING ALL SUBCATEGORIES OF MIXED RS AND LS THROUGH THE GMODS PROCESS.

- To obtain a 10 wt % of Na<sub>2</sub>O in the final glass, 15 wt % Na<sub>2</sub>O (based on the feed) should be added during the glass formation (Fig. 6.12).

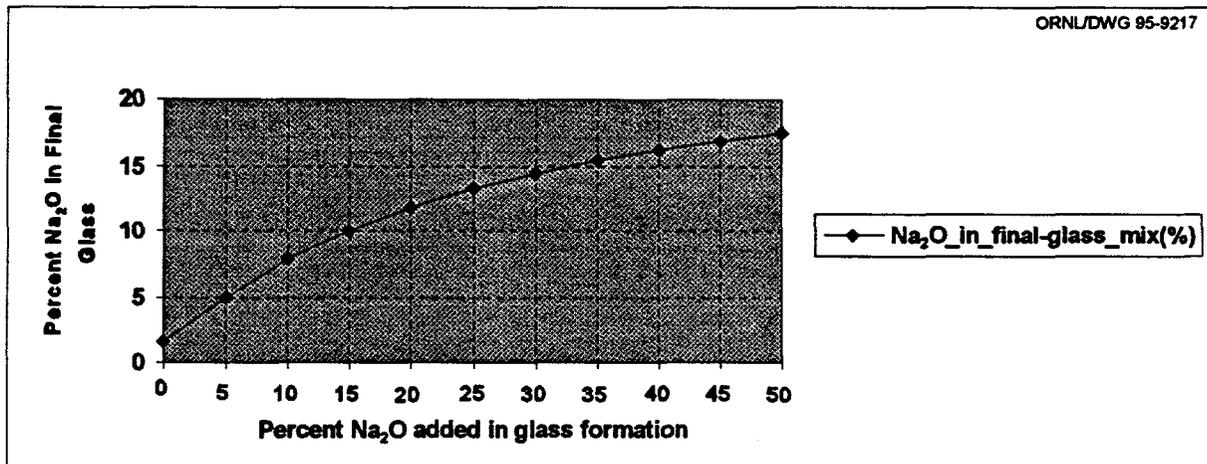


Fig. 6.12. Na<sub>2</sub>O composition in final glass vs percent added during the melting process for RS-LS mix.

- The content of Pu in the initial mixture of RS and LS is about 1.05 wt %. Once treated by the GMODS process, the content of Pu in the final glass is about 0.35 wt % (Fig. 6.13).

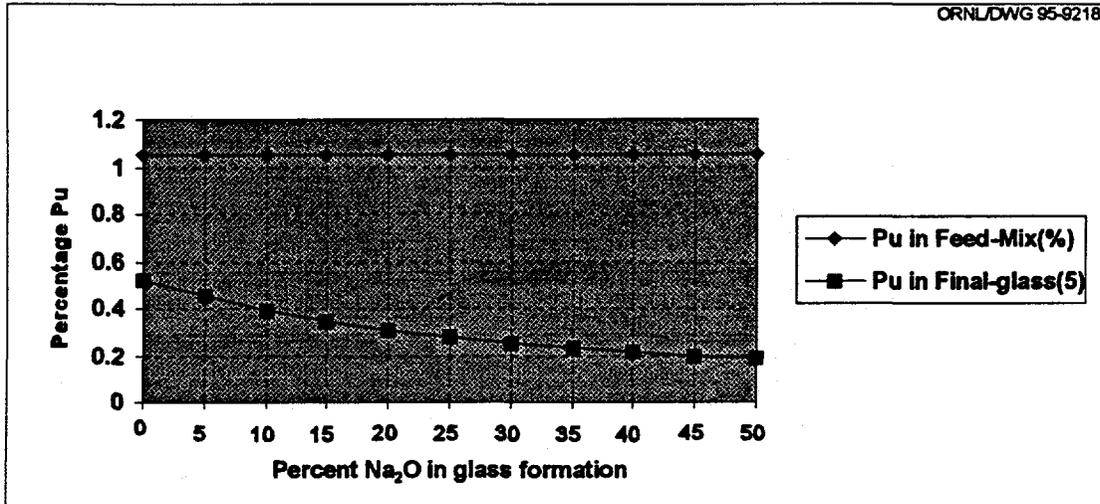


Fig. 6.13. Pu percent in RS-LS mix and final glass formation.

- The initial mass of mixture of RS and LS was about 273,000 kg, resulting in approximately 750,000 kg (268 m<sup>3</sup>) of final glass. The ratio of glass to waste is about 2.75 (Fig. 6.14).

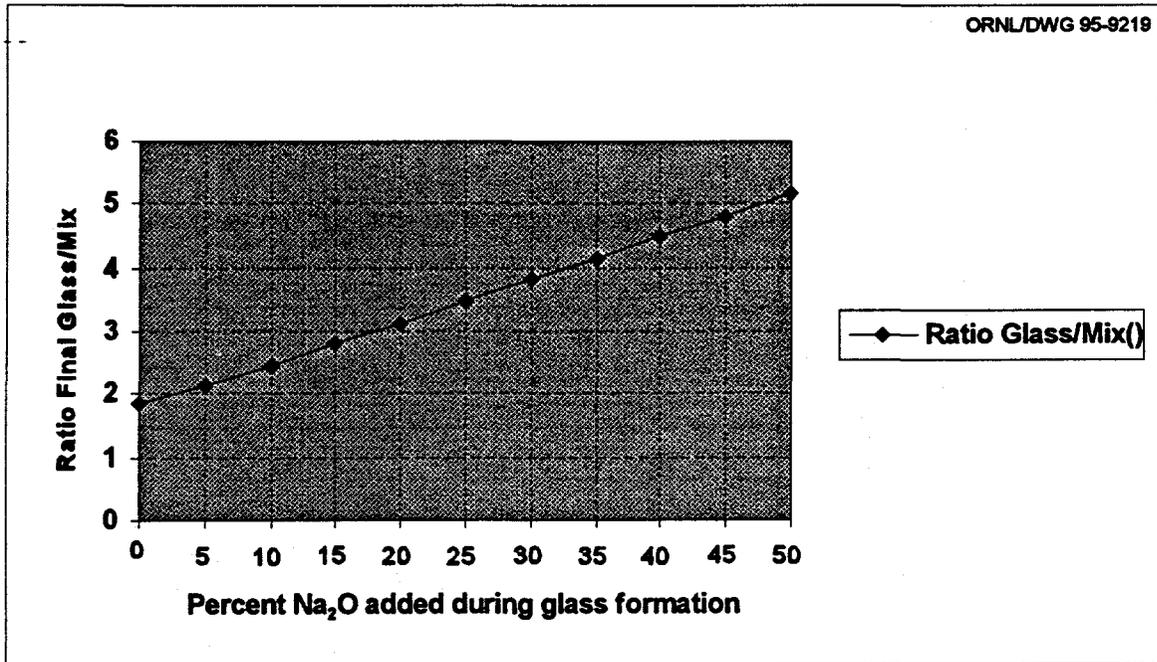


Fig. 6.14. Ratio of final glass to initial RS-LS mixed mass.

- The  $\text{SiO}_2$  added to the glass formation is about 1.25, expressed as the ratio of  $\text{SiO}_2$  added to feed a mixture of RS and LS (Fig. 6.15).

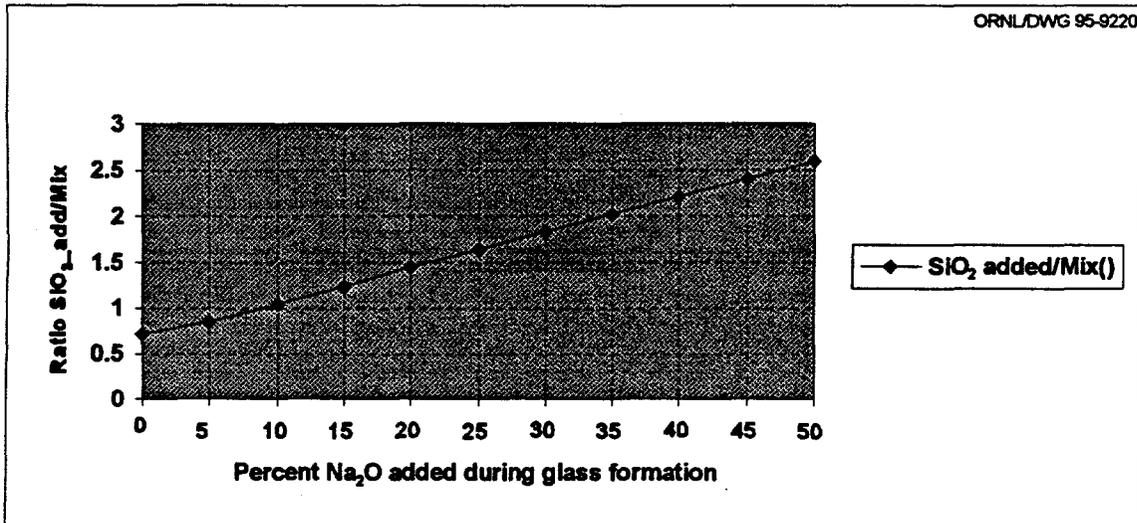


Fig. 6.15. Ratio  $\text{SiO}_2$  to RS-LS mix added during the glass formation process.

- The  $\text{B}_2\text{O}_3$  added to the glass formation is approximately 0.48, expressed as the ratio of  $\text{B}_2\text{O}_3$  added to feed of the mix RS and LS (Fig. 6.16).

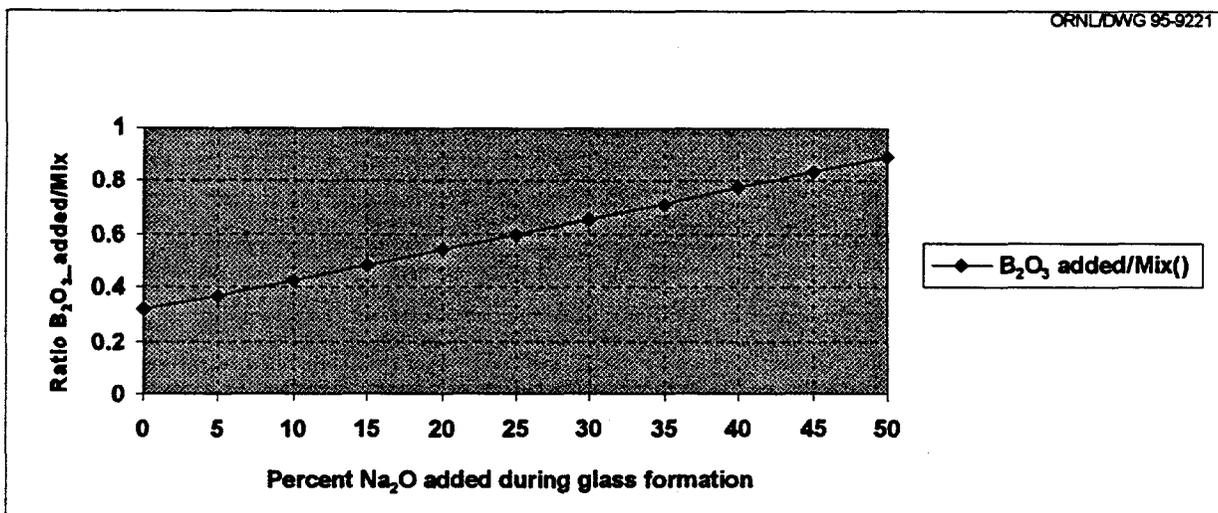


Fig. 6.16. Ratio  $\text{B}_2\text{O}_3$  to RS-LS mix added during the glass formation process.

- The melting temperature was set at approximately 1200°C (Fig. 6.17). The GMODS process can work at this temperature very comfortably.

Mixing all subcategories of RS and LS at once proved to have no major affect on volume reduction. It is clear that mixtures of subcategories could bring benefits in the form of volume reduction. For example, mixing chlorides with ashes may result in interesting volume reduction behavior. The following sections focus on different mixtures of Pu-contaminated waste subcategories.

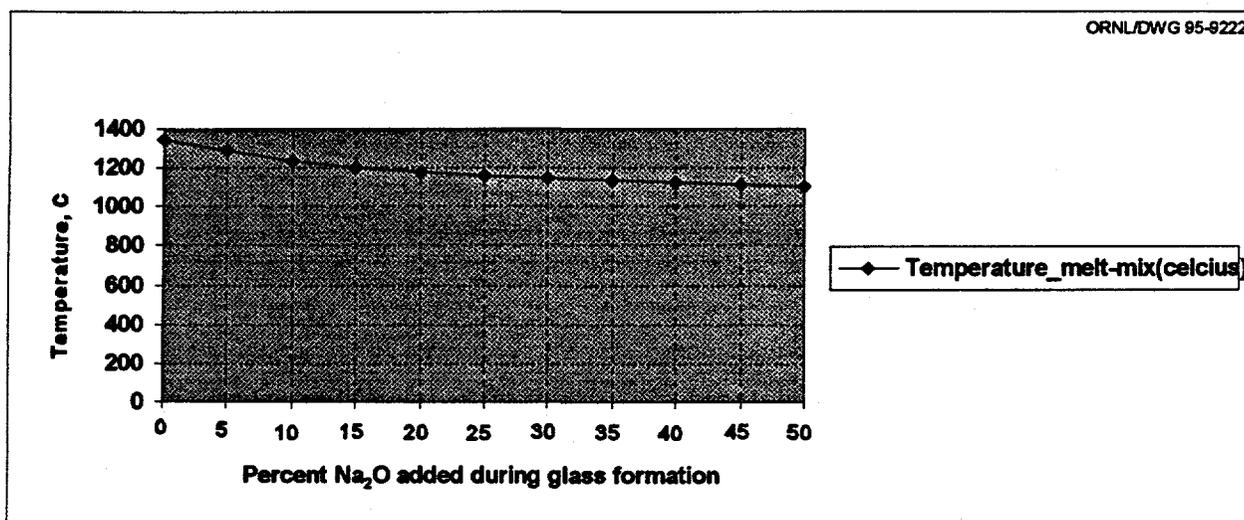


Fig. 6.17. Melting temperature for the RS-LS mix vs Na<sub>2</sub>O added during the glass-formation process.

#### 6.4 RS ASH AND CHLORIDE SALTS BLENDS

To see what effect the blending of various waste streams may have on final glass volume, two of the RS substreams, ash and chlorides salts, were blended together in different combinations. In the first run, both of the waste streams were treated separately. This produced a total final glass mass of 217,500 kg (77.5 m<sup>3</sup>), 28,500 kg from treating the ash stream and 189,000 kg from treating the chloride salt stream. Then two series of runs were performed to study the effects of blending. In the first series, various mixtures of the waste streams were created by combining all of the chloride salts stream and an increasing amount of ash ranging from 10 wt % of the ash stream up to 100 wt % of the ash stream. This blend was then fed to GMODS to produce the final glass product. The remaining ash, which was not used in the mixture, was fed as a separate stream into the GMODS process and also produced a final glass product.

In the second series of tests, the same thing was done—except the blend stream always contained 100 wt % of the ash stream, and the amount of the chloride salt stream added was increased from 10 to 100 wt %. The results from these runs are shown in Table 6.1 and Figs. 6.18 and 6.19.

Looking at Table 6.1, one can see that the first run during which each of the waste streams was treated separately, produced the largest mass of glass, 217,500 kg (77.5 m<sup>3</sup>). The other two series

**Table 6.1 Final glass mass for mixtures of RS ash and chloride salt streams**

Mixture % ash:chlorides	Mass glass from ash (kg)	Mass glass from chlorides (kg)	Mass glass from mixture (kg)	Total glass mass (kg)
0:0	28,500	189,000	0	217,000
10:100	25,700	0	46,400	72,100
20:100	22,800	0	48,500	71,300
30:100	19,900	0	51,100	71,000
40:100	17,100	0	53,600	70,700
50:100	14,200	0	56,200	70,400
60:100	11,400	0	58,700	70,100
70:100	8,540	0	61,200	69,800
80:100	5,700	0	63,800	69,500
90:100	2,850	0	66,300	69,100
100:100	0	0	68,800	68,800
100:100	0	170,000	31,400	202,000
100:200	0	151,000	34,900	186,000
100:300	0	132,000	38,800	171,000
100:400	0	113,000	42,800	156,000
100:500	0	94,500	47,100	142,000
100:600	0	75,600	51,500	127,000
100:700	0	56,700	55,800	112,000
100:800	0	37,800	60,200	97,900
100:900	0	18,900	64,500	83,400

of runs show that mixing the two waste streams causes a decrease in the final waste mass down to as low as 68,800 kg (24.6 m<sup>3</sup>) when the two streams are completely mixed. For the first series, Fig. 6.18 shows the affect of adding increasing amounts of ash to the chloride salt stream. In that case, the final mass of the glass produced from the mixture and the unmixed ash is reduced to about

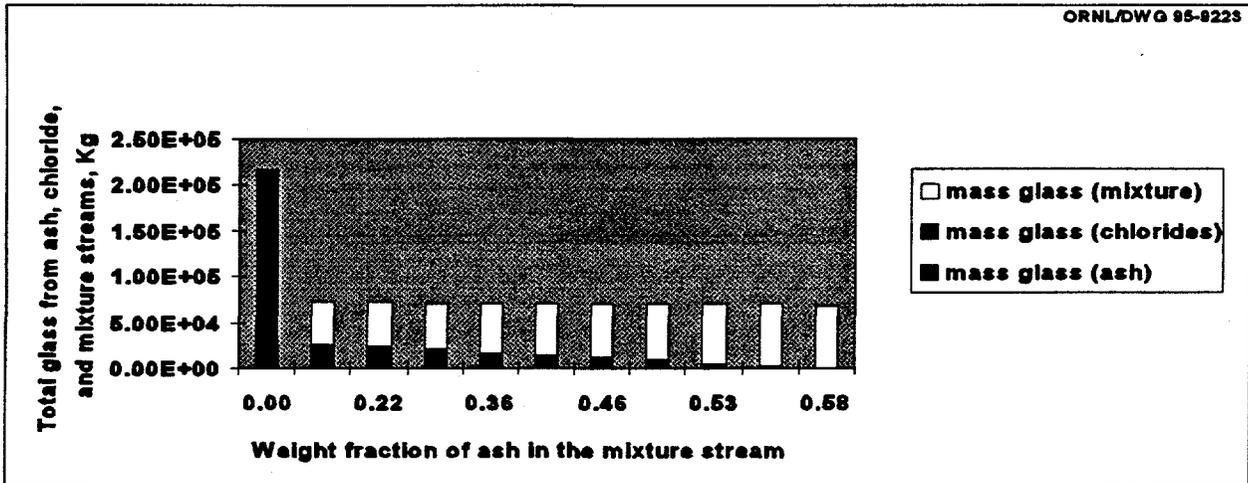


Fig. 6.18. Effect on glass produced from addition of ash to chloride salt stream.

70,000 kg (25 m<sup>3</sup>) with just 10 wt % addition of ash to the chloride salt stream. The final glass mass stays at about that same level—no matter how much more ash is added. The reason for this phenomenon is that the ash stream is made up of almost 45 wt % SiO<sub>2</sub>. When the ash is added to the chloride salt stream, the amount of SiO<sub>2</sub> that is required to be added in the GMODS process is decreased. In fact, the first 10 wt % addition of the ash stream provides enough SiO<sub>2</sub> for all the chloride salt stream and any additional ash added has little additional effect.

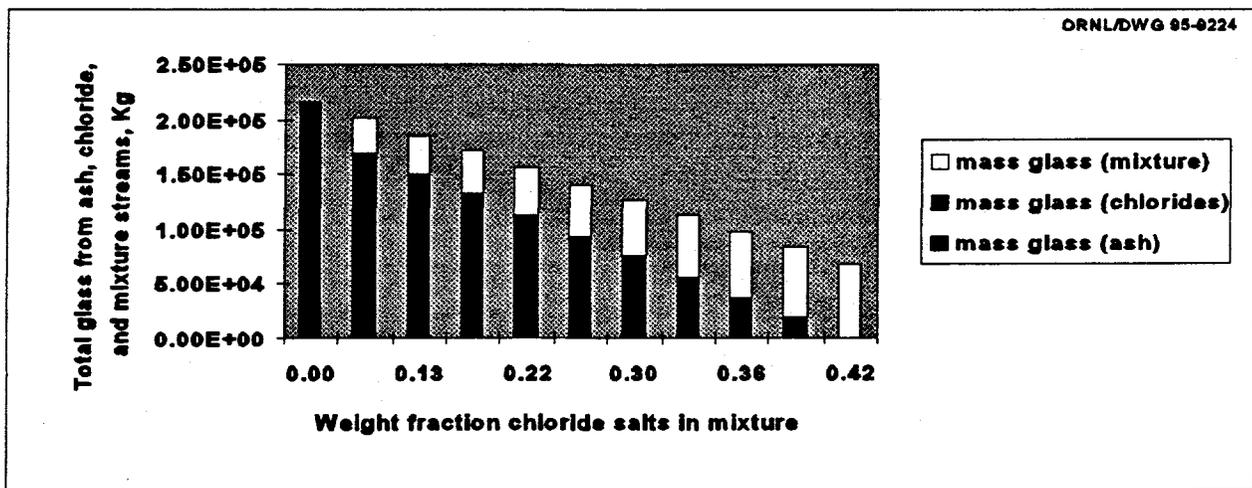


Fig. 6.19. Effect on glass produced from addition of chloride salt stream to the ash stream.

In the second series of tests, the effect of adding part of the chloride salt stream to the ash stream can be seen in Fig. 6.19. The largest volume of waste is again from the treatment of the two waste streams separately with the majority of the glass produced by treating the chloride salt stream alone. As in the first series of runs, as you combine the two waste streams the final volume decreases. However, in this case it does not decrease as rapidly. As one adds the chloride salt stream to the ash stream, that portion of the chloride salt stream no longer requires additional amounts of  $\text{SiO}_2$ ; therefore, the final mass is decreased. However, the remaining part of the chloride salt stream still requires additional  $\text{SiO}_2$ , and this produces the largest mass of glass. So, in this series, the total combined volume of the two treated streams continues to decrease as more and more chloride salts is added to the ash and increasingly less  $\text{SiO}_2$  is required for the remaining chloride salt stream.

### **6.5 EFFECT OF TEMPERATURE AND $\text{Na}_2\text{O}$ ADDITION IN VOLUME REDUCTION FOR LS SUBCATEGORIES**

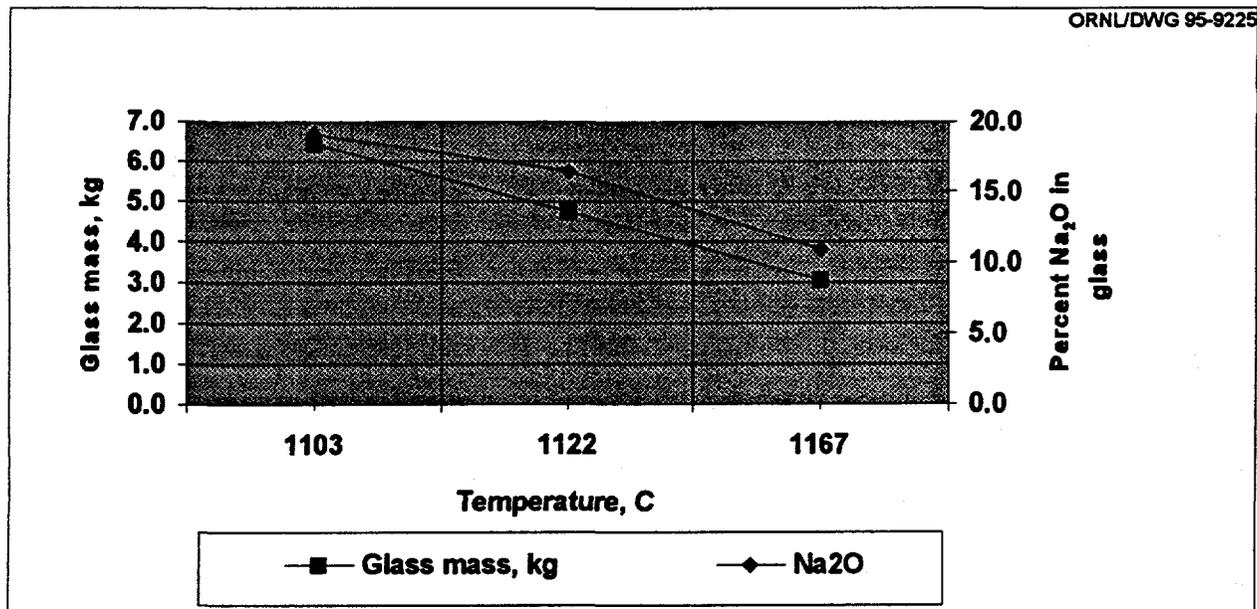
During the melting process, two variables modify the viscosity of the forming glass. Temperature increase and adding  $\text{Na}_2\text{O}$  each produce a reduction in viscosity. For furnaces in which the temperature is a limitation, the preferred option for a viscosity reduction would be an increase of the amount of  $\text{Na}_2\text{O}$ . However, the negative side of this addition would be the increase in the final volume of glass. For processes in which the temperature is not such a limiting parameter—for example, the GMODS process—it is better to increase the temperature and reduce the amount of  $\text{Na}_2\text{O}$  producing a smaller amount of final glass.

As an example, let us consider Fig. 6.20, which presents results of an analysis of glass formation for the LS subcategory chlorides. Assuming that the process start with 1 kg of chlorides, the melting point reaches  $1103^\circ\text{C}$ , and the corresponding  $\text{Na}_2\text{O}$  concentration is about 20 wt %. The resulting final glass mass is about 6.5 kg. If the temperature is allowed to increase to about  $1167^\circ\text{C}$  the final glass mass is about 3 kg. By changing the temperature to  $64^\circ\text{C}$ , there is a reduction of about 50 wt % in the final glass mass. This is an important consideration that may impact the melting process during the glass formation.

Similar effects are observed with other subcategories of LS. Table 6.2 shows each of the other LS subcategories and the mass reduction for a respective temperature increase. Table 6.2 also shows the decrease in the percent of  $\text{Na}_2\text{O}$  in the final glass. Curves illustrating the specific LS subcategories are illustrated in Appendix D.

### **6.6 EFFECTS OF TEMPERATURE AND $\text{Na}_2\text{O}$ ADDITION ON VOLUME REDUCTION FOR RS SUBCATEGORIES**

The modeling of the glass formation using RS subcategories shows similar results to that of the previous subsection in which during the melting process there were two variables that modified the



**Fig. 6.20. Effects of temperature and Na<sub>2</sub>O on the final glass mass.**

viscosity of the forming glass. Temperature increase and adding Na<sub>2</sub>O, respectively, produced a reduction in viscosity.

For example, consider Fig. 6.21, which presents results from an analysis of glass formation for the RS subcategory sludges. Assuming that the process starts with 1 kg of sludges, the melting point reaches 1064°C and the corresponding Na<sub>2</sub>O concentration is about 18 wt %. The resulting final glass mass is about 4.8 kg. If the temperature is allowed to increase to about 1157°C the final glass mass is about 2.3 kg. If we change the temperature to 97°C, there is a reduction to about 52 wt % in the final glass mass.

Similar effects are observed with other subcategories of RS. Table 6.3 shows each one of the other RS subcategories and the mass reduction for a respective temperature increase. This table also shows the decrease in the percent of Na<sub>2</sub>O in the final glass. Curves illustrating the specific LS subcategories are illustrated in Appendix D.

**Table 6.2 Effect of temperature on mass reduction for LS glass formation**

Subcategory	Temperature increase	Na <sub>2</sub> O decrease	Mass reduction, weight percent of larger mass
Chlorides	64	9	53
Combustibles	105	8.5	54
Graphite	66	10	52
Grit	25	13	52
Heels	47	10	54
Resins	180	11	53
Sludges	82	10	51
Scrap metals	195	10	50
Insulation	36	16	45
SS&C	38	10	54
Firebricks	77	10	56
Crucibles	45	10	55
Lead gloves	No good glass produced	By sending only this subcategory	A percentage of >25 wt % of PuO <sub>2</sub> is in the glass
Ash	10	2.3	9
Glass	48	13	50

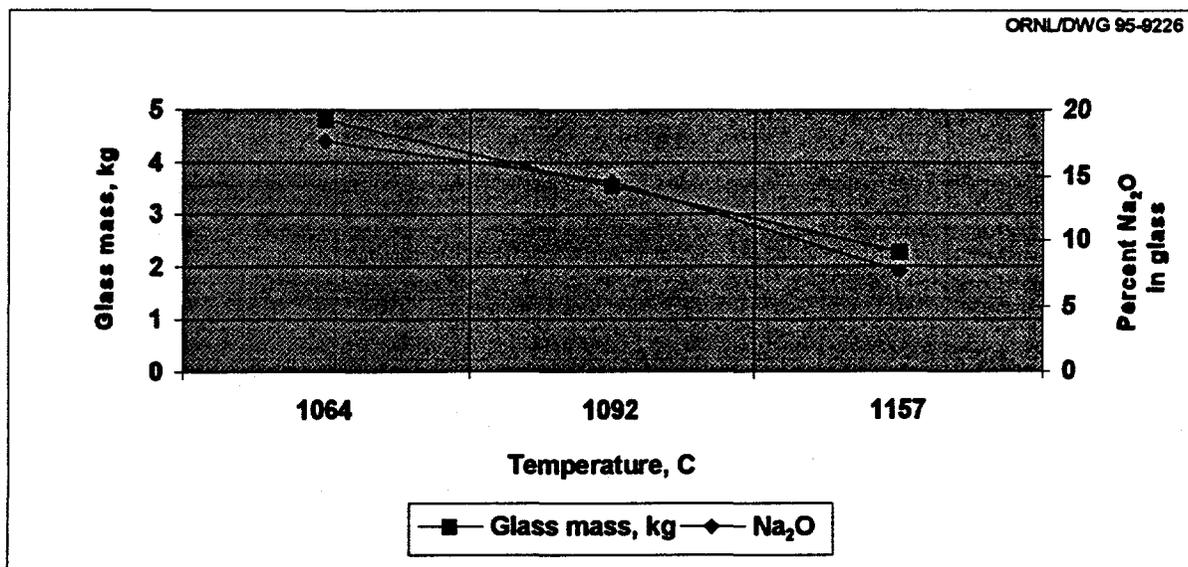


Fig. 6.21. Effects of temperature and Na<sub>2</sub>O on the final glass mass for sludge (RS).

Table 6.3 Effect of temperature on mass reduction for RS glass formation

Subcategory	Temperature increase	Na <sub>2</sub> O decrease	Mass reduction, weight percent on larger mass
Sludge	93	10	54
SS&C	43	10	50
Insulation	120	13	48
Chlorides	79	9	56
Crucibles	53	9	55
Ash	55	8	41

## 7. ANALYSIS

Simulation of the GMODS process using FLOW has been successful. The information given by the GMODS experts and obtained from different publications written by the GMODS authors was translated first in a step-by-step flowsheet process and then put into FLOW, a simulation program developed by J. J. Ferrada et al. This simulation was used to analyze the time-averaged material flows, compositions, conformance to specifications, and product quality of GMODS for a variety of plant feed materials. A number of simplifications and assumptions were incorporated into the model that facilitated the calculations. FLOW treated the GMODS process as a steady-state, continuous process. Since the interest was focussed in time-averaged flows from the process rather than instantaneous conditions, this was a good approximation. Although the various steps of the GMODS process were described as taking place in a single vessel, an induction furnace, the FLOW model of GMODS was sequenced through a FLOWsheet of unit operations connected by streams. Since the interest for this study is not focussed on time and space behavior inside the vessel, this is a reasonable assumption. Also, reaction equilibria were assigned by the analyst, and the residence/time in the vessel was assumed to be sufficient such that an assumed extent of reaction was achieved.

The glass formation model was divided into two submodels. The first submodel analyzed whether the glass formed was within the appropriate glass formation region according the boro-silica glass system obtained from publications from Clemson University.<sup>7, 12</sup> The other submodel analyzed some properties of the glass such as viscosity and  $\Delta G$  of formation. Glasses not within an acceptable range for these properties are modified by adding  $\text{Na}_2\text{O}$  or by increasing the temperature.

Waste streams used in this report are from the LLNL document, *Pretreatment Process for Immobilization Initial Report*, which was written as part of the SFM Control and Disposition Program. Information for these streams was obtained from the NMMSS database and from the DOE sites. We used the same categories as listed in the LLNL report. The waste stream data were broken into 11 separate feed streams. These feed streams correspond to the eleven major material categories that are typically used in the DOE complex.

Simulation of the GMODS process included several cases in which variations were made to the input feed. First, the system was fed with all the subcategories of RS at once. Second, the system was fed with all the subcategories of LS at once. Third, the system was fed with the combination of all the subcategories of RS and LS at once. Fourth, to observe the effect of blending various waste streams on final glass volume, two of the RS substreams, ash and chlorides salts, were blended in different combinations. Fifth, volume reduction was analyzed by altering the amount of  $\text{Na}_2\text{O}$  added and by changing the temperature of melting.

Evaluation of the treatment of the RS and LS waste streams shows that the GMODS process treats both streams separately or combined to form durable, glass waste forms. In general terms, it may be said that the mixture of subcategories is very attractive for volume reduction. Additions to this study should include analysis of all possible mixtures and their respective effect on volume reduction.

This study has shown that a major parameter affecting the final glass volume is the temperature of the melt, when operating within a given viscosity. Volume reductions of about 50% was obtained for the borosilicate glass developed by SRL. For example, when 1 kg of chloride salts was processed, the temperature was at 1103°C and produced 6.5 kg of glass at a given viscosity. However, when the temperature was increased to 1167°C, the final glass mass decreased to about 3 kg at the same viscosity. This increase in temperature is not a problem for the GMODS process. A complete set of results were presented in Appendix D, including tables that show glass compositions for various rich and lean Pu scrap and residue waste streams as a function of the melting temperature. More extensive analysis should be conducted to determine maximum increases in temperature and their effect on volatilization of some heavy metals. Experimental investigations should include studies for the extent of reactions during the glass formation process and also determine the conditions under which Pu is more likely to be transferred to the gas phase.

The composition of the various waste streams were presented in Appendix B. These tables have been compiled from several reports and also heuristics when information was not directly available. Further waste characterization is required for greater accuracy of the results. This is particularly true for those waste streams that were not analyzed in this study.

As was mentioned previously, the model of GMODS has been based on the boro-silicate model developed at SRL. Separate experiments are currently being conducted by glass experts for the GMODS process. The current FLOW model of the GMODS process requires validation and verification based on such experimental results. The next step in completing the modeling of the GMODS process will be the incorporation of this information into the FLOW model.

In summary, the simulation of the GMODS process showed that the glass chemistry postulated in the models produces an acceptable glass. It is expected that the glass chemistry assumed during the modeling process can be verified with laboratory experiments currently being conducted relating to the GMODS process. Further waste characterization, especially of the SFM waste streams not studied in this report, will provide more nearly accurate results and facilitate a more detailed evaluation of the GMODS process.

This initial assessment shows that the GMODS process works within an acceptable level of confidence based on similar glass processes used for high level waste. Furthermore, GMODS could treat the SFM waste streams and it can be forecasted that the process will save money due to its simplicity and flexibility for treating different types of wastes.

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**Appendix A**

**WASTE CHARACTERIZATION**



**Table A.1. LS and RS scrap stream definition**

Material category	Wt % Pu	Mass Pu (kg)	Total mass (kg)
<b><i>LS</i></b>			
Ash	0.17	13.00	7,275
Ceramic crucibles	0.11	3.00	2,617
Chloride salts/chloride containing oxides	0.27	18.00	6,443
Combustibles	0.30	63.00	21,221
Firebrick-LECO	1.36	178.00	13,092
Glass	0.05	12.00	25,261
Graphite	0.10	23.00	23,879
Grit blasting residues	0.03	0.00	1,040
Heels	1.40	2.00	136
Insulation, filters	0.25	48.00	18,867
Ion exchange resins	0.12	2.00	1,547
Leaded gloves	0.04	7.00	16,262
Nonconforming	0.00	0.00	3,424
Sand, slag, and crucible	0.52	15.00	2,883
Scrap metal	0.05	39.00	75,330
Sludges	0.02	1.00	6,218
Solutions	Unknown	Unknown	Unknown
Total	0.19	423.00	225,495
<b><i>RS</i></b>			
Ash	5.13	970.00	18,926
Ceramic crucibles	2.63	46.00	1,750
Chloride salts/chloride-containing oxides	7.99	1,084.00	13,566

**Table A.1. LS and RS scrap stream definition (continued)**

<b>Material category</b>	<b>Wt % Pu</b>	<b>Mass Pu (kg)</b>	<b>Total mass (kg)</b>
Graphite	5.69	175.00	3,079
Insulation, filters	4.40	94.00	2,133
Plutonium fluorides	Unknown	Unknown	Unknown
Sand, slag, crucible	4.30	126.00	2,932
Sludges	4.26	26.00	611
Solutions	Unknown	Unknown	Unknown
<b>Total</b>	<b>5.86</b>	<b>2,521.00</b>	<b>42,997</b>

Table A.2a. Synonyms for RS waste streams

Substream	Component	Wt %
Ash	Pu	5.13
	SiO <sub>2</sub>	45.00
	C	20.00
	Al <sub>2</sub> O <sub>3</sub>	7.00
	CaO	7.00
	Fe <sub>2</sub> O <sub>3</sub>	7.00
	Na <sub>2</sub> O	5.87
	Pb	2.00
	Cr	1.00
Crucibles	Pu	1.63
	PuO <sub>2</sub>	1.00
	MgO	35.00
	ZrO	9.37
	Al <sub>2</sub> O <sub>3</sub>	30.00
	CaCl <sub>2</sub>	1.00
	NaCl	1.00
	Kcl	1.00
	SiO <sub>2</sub>	20.00
Chloride_salts	PuO <sub>2</sub>	7.99
	NaCl	22.10
	MgCl <sub>2</sub>	22.00
	CaCl <sub>2</sub>	22.00

**Table A.2a. Synonyms for RS waste streams (continued)**

Substream	Component	Wt %
	KCl	23.00
	Am	1.00
	ZnCl <sub>2</sub>	2.00
<b>Graphite</b>		
	Pu	5.69
	CaF <sub>2</sub>	1.00
	C	91.31
	Ca	0.50
	Mg	0.50
	MgO	0.50
	CaO	0.50
<b>Insulation</b>		
	Pu	4.40
	Al	48.00
	SiO <sub>2</sub>	47.60
<b>Pu Fluorides</b>		
	PuF <sub>4</sub>	97.00
	C <sub>3</sub> H <sub>7</sub> O	3.00
<b>SS&amp;C</b>		
	Pu	4.80
	CaF <sub>2</sub>	8.00
	MgO	80.70
	PuF <sub>4</sub>	0.50
	Ca	3.00
	Mg	3.00

Table A.2a. Synonyms for RS waste streams (continued)

Substream	Component	Wt %
Sludge	Pu	4.30
	H <sub>2</sub> O	25.00
	Fe	10.00
	Np	0.10
	U	0.30
	Fe <sub>2</sub> O <sub>3</sub>	10.00
	SiO <sub>2</sub>	8.00
	MgO	15.00
	C <sub>3</sub> H <sub>7</sub> O	10.00
	C <sub>3</sub> H <sub>8</sub>	5.00
	C	2.00
	CH <sub>4</sub>	5.00
	C <sub>6</sub> H <sub>5</sub> Cl	5.30
Solution	H <sub>2</sub> O	90.00
	HNO <sub>3</sub>	10.00

Table A.2b. Synonyms for LS waste streams

Substream	Component	Wt %
Ash	Pu	0.17
	SiO <sub>2</sub>	45.96
	C	24.00
	Al <sub>2</sub> O <sub>3</sub>	7.00
	CaO	7.00
	Fe <sub>2</sub> O <sub>3</sub>	7.00
	Na <sub>2</sub> O	5.87
	Pb	2.00
	Cr	1.00
Crucibles	Pu	0.06
	PuO <sub>2</sub>	0.05
	MgO	37.00
	ZrO	9.89
	Al <sub>2</sub> O <sub>3</sub>	30.00
	CaCl <sub>2</sub>	1.00
	NaCl	1.00
	KCl	1.00
	SiO <sub>2</sub>	20.00
Chloride_salts	PuO <sub>2</sub>	0.27
	NaCl	23.97
	MgCl <sub>2</sub>	23.92
	CaCl <sub>2</sub>	24.92
	KCl	24.92

Table A.2b. Synonyms for LS waste streams (continued)

Substream	Component	Wt %
	Am	0.20
	ZnCl <sub>2</sub>	1.80
<b>Combustibles</b>		
	Pu	0.30
	C	18.00
	H <sub>2</sub> O	5.00
	CH <sub>4</sub>	20.00
	N <sub>2</sub>	0.70
	C <sub>6</sub> H <sub>5</sub> Cl	24.00
	SiO <sub>2</sub>	5.00
	Al <sub>2</sub> O <sub>3</sub>	7.00
	Fe <sub>2</sub> O <sub>3</sub>	5.00
	O <sub>2</sub>	10.00
	S	5.00
<b>Firebrick</b>		
	Pu	1.36
	MgO	10.64
	SiO <sub>2</sub>	20.00
	CaCO <sub>3</sub>	5.00
	Al <sub>2</sub> O <sub>3</sub>	52.00
	Am	1.00
	CaO	10.00
<b>Glass</b>		
	Pu	0.05

**Table A.2b. Synonyms for LS waste streams (continued)**

Substream	Component	Wt %
	SiO <sub>2</sub>	88.95
	Pb	3.00
	B	8.00
<b>Graphite</b>		
	Pu	0.10
	CaF <sub>2</sub>	1.59
	C	98.31
	Mg	0.50
	MgO	0.50
	Ca	0.50
	CaO	0.50
<b>Grit</b>		
	Pu	0.03
	SiO <sub>2</sub>	80.07
	Al <sub>2</sub> O <sub>3</sub>	9.00
	MgO	10.00
<b>Heels</b>		
	Pu	1.40
	C <sub>3</sub> H <sub>7</sub> O	10.00
	MgO	23.00
	HNO <sub>3</sub>	8.00
	CaO	6.00
	Fe <sub>2</sub> O <sub>3</sub>	6.00
	Al <sub>2</sub> O <sub>3</sub>	7.00

**Table A.2b. Synonyms for LS waste streams (continued)**

Substream	Component	Wt %
	SiO <sub>2</sub>	18.00
	NaCl	5.20
	KCl	5.20
	C <sub>3</sub> H <sub>8</sub>	5.20
	C	5.00
Insulation	Pu	0.25
	Al	50.10
	SiO <sub>2</sub>	49.65
Resins	Pu	0.12
	C	30.00
	H <sub>2</sub>	9.88
	Na	60.00
Pb_gloves	Pu	0.04
	Pb	10.00
	C	50.00
	H <sub>2</sub>	5.00
	O <sub>2</sub>	30.00
	N <sub>2</sub>	4.62
	S	0.34
Nonconforming	Pu	0.00

**Table A.2b. Synonyms for LS waste streams (continued)**

Substream	Component	Wt %
	CaCO <sub>3</sub>	10.00
	Fe <sub>2</sub> O <sub>3</sub>	10.00
	MgO	10.00
	H <sub>2</sub> O	40.00
	CH <sub>4</sub>	10.00
	C	20.00
SS&C	Pu	0.52
	CaF <sub>2</sub>	8.00
	MgO	81.48
	Ca	5.00
	Mg	5.00
Scrap_metal	Pu	0.05
	Fe	65.00
	Fe <sub>2</sub> O <sub>3</sub>	25.00
	Cu	2.00
	Al	7.00
	Al <sub>2</sub> O <sub>3</sub>	0.95
Sludge	Pu	0.02
	H <sub>2</sub> O	25.28
	Fe	11.00
	Np	0.10
	U	0.30

**Table A.2b. Synonyms for LS waste streams (continued)**

Substream	Component	Wt %
	Fe <sub>2</sub> O <sub>3</sub>	10.00
	SiO <sub>2</sub>	8.00
	MgO	15.00
	C <sub>3</sub> H <sub>7</sub> O	10.00
	C <sub>3</sub> H <sub>8</sub>	6.00
	C	3.00
	CH <sub>4</sub>	5.00
	C <sub>6</sub> H <sub>5</sub> Cl	6.30
Solutions	H <sub>2</sub> O	90.00
	HNO <sub>3</sub>	10.00



**Appendix B**

**EMPIRICAL CORRELATIONS FOR PREDICTING GLASS DURABILITY**



## B.1 SILICON RELEASE AS A FUNCTION OF FREE ENERGY OF HYDRATION (4-WEEK STATIC MCC-1 LEACH TEST)

This approach predicts glass durability from glass composition based upon thermodynamic hydration equations which represent the glass dissolution mechanisms of ion exchange and matrix dissolution. The leaching of silicate and boro-silicate glasses containing alkali or alkaline earth elements is known to be autocatalytic in that the initial ion exchange of alkali in the glass for hydrogen ions in water results in the formation of OH and increases the pH of the leachate. The increased pH then increases the rate of silicate network attack, thus accelerating the leaching effect. In this approach, the correlation equation relating glass composition to silicon and boron released from the glass was expressed as:<sup>1</sup>

$$\log Si(g/m^2) = -0.1636 \Delta G_{hyd} + 0.3557, \quad R^2=0.73, \quad (1)$$

and

$$\log B(g/m^2) = -0.1648 \Delta G_{hyd} + 0.3557, \quad R^2=0.73, \quad (2)$$

respectively.

Log  $Si$  and Log  $B$  represent leachant concentrations of Si and B, respectively, on exposed glass-surface area. These concentrations were normalized to the amount of Si and B in the respective glass. In  $\Delta G_{hyd}$  represents the glass free energy of hydration in kcal/mol. Both equations relate the composition of Si and B to the pH corrected  $\Delta G_{hyd}$ .

$\Delta G_{hyd}$  can be calculated from the analyzed glass compositions alone and from a combination of the glass compositions and the final solution pH. By monitoring boron release with his approach, a worst-case release can be calculated for nuclear waste glasses in order to satisfy the waste acceptance preliminary specification (WAPS) 1.3 because boron is released from the glass at a greater rate than any radionuclide.

## B.2 GLASS DISSOLUTION RATE AS A FUNCTION OF LEACHATE pH (1-WEEK PCT TEST)

A previous study within the portion of the  $Na_2O-B_2O_3-SiO_2-Al_2O_3-Fe_2O_3-CaO$  system showed that long-term glass dissolution (PCT Test) is a function of both glass composition and associated glass structural ratios.<sup>2</sup>

For glasses with  $SiO_2/B_2O_3$  ratio  $> 5$ ,

$$g R_{Na} (mg/L/cm^2s^2) = 0.51L - 18.2275 \quad \text{for } 10.5 < L < 13 \quad (3)$$

where  $R_{Na}$  is the dissolution rate of sodium and  $L$  is the pH value of leachate.

For glasses with  $\text{SiO}_2:\text{B}_2\text{O}_3$  ratio  $\leq 5$  (boro-silicate glass),

$$\log NR_{Na} \text{ (mg/l)} = 2.34 - 0.11(\Delta G_{pH}) , \quad (4)$$

where  $NR_{Na}$  is the 1-week PCT sodium release from the glass and  $\Delta G_{pH}$  is the pH-corrected free energy of hydration of the glass.

### B.3 CANONICAL CORRELATION OF WASTE GLASS COMPOSITIONS AND DURABILITY (1-WEEK PCT TEST)<sup>3</sup>

In a previous study, the 1-week PCT leach test results of a statistically balanced composition set of 30 samples in the Si-B-Na-Ca-Al-Fe-O system was analyzed using canonical correlation methods. We have two subsets of variables,  $x$  and  $y$ , where  $x$  has seven durability measures  $[x_1, \dots, x_7]$ , namely [Si, B, Na, Ca, Al, Fe, pH];  $x_1$  to  $x_6$  represents the metal release from the glass in parts per million, and  $x_7$  is the pH value of leachate. On the other hand,  $y$  has a measure of seven oxide mole fraction measures  $[y_1, \dots, y_7]$ , namely  $[\text{SiO}_2, \text{Al}_2\text{O}_3, \text{B}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{FeO}, \text{CaO}, \text{Na}_2\text{O}]$ . Canonical correlation was used to relate the dependent variable set  $x$  and independent variable set  $y$ . Through complex calculation procedures, two matrices were obtained:

$A =$	-0.601	0.149	-0.735	0.035	1.000	-0.074	-0.499
	-0.284	-0.395	-0.971	0.471	-0.203	0.02	-0.476
	1.000	-0.305	1.000	0.578	-0.719	0.208	1.000
	0.229	-0.461	0.322	0.244	0.040	1.000	-0.031
	-0.414	0.704	0.203	1.000	-0.012	0.261	0.014
	-0.072	0.485	-0.513	-0.158	-0.004	0.866	0.039
	0.778	1.000	0.250	-0.186	-0.003	-0.162	-0.121
and							
$B =$	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	0.986	0.987	0.971	0.981	0.973	0.975	0.977
	0.858	0.843	0.857	0.859	0.852	0.856	0.854
	0.767	0.765	0.758	0.734	0.758	0.761	0.778
	0.248	0.262	0.259	0.269	0.254	0.255	0.232
	0.878	0.889	0.885	0.889	0.888	0.89	0.887
	0.963	0.987	0.976	0.988	0.971	0.974	0.972

The first canonical variate for the first set of dependent variables,  $x$ , from  $A$  is:

$$a_1'x = -0.601 Si - 0.284B + Na + 0.229 Ca - 0.414 Al - 0.0 \quad (5)$$

Similarly the first canonical variate for the first set of independent variables,  $y$ , from  $B$  is:

$$b_1'y = SiO_2 + 0.986 Al_2O_3 + 0.858 B_2O_3 + 0.767 Fe_2O_3 + 0.248 FeO + 0. \quad (6)$$

and there is a linear relation between  $a_1'x$  and  $b_1'y$ :

$$a_1'x = -5 b_1'y \quad (7)$$

If glass composition is known ( $SiO_2$ ,  $Al_2O_3$ ,  $B_2O_3$ ,  $Fe_2O_3$ ,  $FeO$ ,  $CaO$ , and  $Na_2O$ ), the release rates of Si, B, Na, Ca, Al, Fe from the glass and the leachate pH can be calculated by combining Esqs. (5) to (7).

The method is complex and could be better understood by reading the reference paper.<sup>3</sup> Copies of the document can also be obtained from the authors of this report.

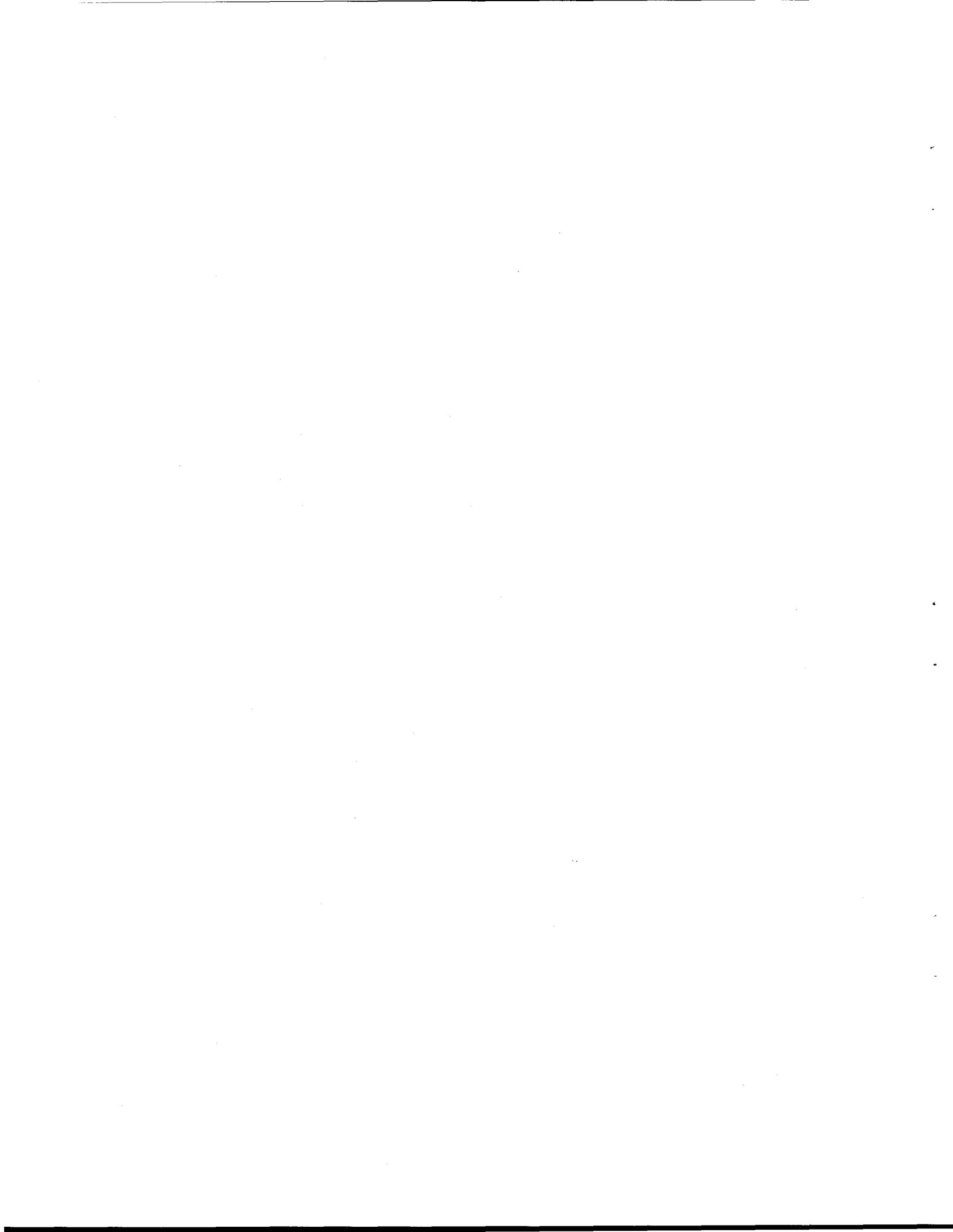
### B.3. REFERENCES FOR APPENDIX B.

1. C. M. Jantzen, "First Principles Process-Product Models for Vitrification of Nuclear Waste: Relationship of Glass Composition to Glass Viscosity, Resistivity, Liquidus Temperature, and Durability," *Nuclear Waste Management IV, Ceramic Transaction*, Vol. 23, 1992, pp. 37-51.
2. William B. Ramsey, C. M. Jantzen, and T. D. Taylor, *Relationship Between Boro-silicate Glass Composition, Structure, and Durability Test Response*, Westinghouse Savannah River Technology Center, Aiken, South Carolina, 1994.
3. D. Oksoy, W. G. Ramsey, D. F. Bickford, and L. D. Pye, "Canonical Correlation of Waste Glass Compositions and Durability, including pH," Westinghouse Savannah River Technology Center, Aiken, South Carolina, December 1994.



**Appendix C**

**DATA FILES USED IN THE  
GMODS SIMULATION**



**FILE: GLASS.DB**

- \* This is the ternary phase diagram database for the formation of glass.
- \* The "C-point" is by convention the waste that one is trying to contain.
- \*
- \* The coordinates of the ellipse must be in a clockwise or counterclockwise direction. The starting point doesn't matter. In other words, do not enter in points across from each other.
- \*

{ B2O3 SiO2 R2O TERNARY GLASS SYSTEM

A: SiO2 --> SiO2 , Al2O3

B: B2O3 --> B2O3

C: R2O --> rest

COORDINATES OF ELLIPSE (DIAMOND): FORMAT: A % B % C % = 100%

1) A 72 B 7 C 21

2) A 65 B 17 C 18

3) A 54 B 24 C 22

4) A 61 B 12 C 27

}

{ Na2O SiO2 R2O TERNARY GLASS SYSTEM

A: SiO2 --> SiO2 , Al2O3 , Fe2O3

B: Na2O --> Na2O , Li2O , K2O , Cs2O

C: RO --> rest

COORDINATES OF ELLIPSE (DIAMOND): FORMAT: A % B % C % = 100%

1) A 50 B 50 C 0

2) A 80 B 20 C 0

3) A 80 B 0 C 20

4) A 50 B 30 C 20

}

**FILE: GLASS.CPD**

- \*\* This file contains a list of compounds and their maximum weight percents
- \*\* allowed in a glass from three IDMS demo at SRS
- \*\* format is NAME WEIGHT%(lower limit) WEIGHT%(upper limit)

TiO2 0.0 1.0

Cr2O3 0.0 3.0

P2O5 0.0 0.3

Fe+2 0.1 0.5

Fe+3 0.1 0.5

**FILE: C\_PbO.RXN**

1

C PbO 12 223.2 12 CO2 Pb - - 44 207.2 0 0 1200 1.0 99

**FILE: NaOH\_Cl.RXN**

2

NaOH PbCl2 40 278.1 21 NaCl Pb(OH)2 - - 58.45 241.2 0 0 2100 1.0 99

NaOH PbF2 40 245.2 21 NaF Pb(OH)2 - - 42 241.2 0 0 2100 1.0 99

**Table C.1 Category Composition of Lean and Rich Scrap (wt %)**

	LS	RS
<b>MASSFLOW(kg)</b>	<b>225,495.00</b>	<b>42,997.00</b>
<b>Ash</b>	<b>3.22</b>	<b>44.00</b>
<b>Crucibles</b>	<b>1.16</b>	<b>4.10</b>
<b>Chloride salts</b>	<b>2.85</b>	<b>31.50</b>
<b>Combustibles</b>	<b>9.41</b>	<b>0.00</b>
<b>Firebrick</b>	<b>5.80</b>	<b>0.00</b>
<b>Glass</b>	<b>11.20</b>	<b>0.00</b>
<b>Graphite</b>	<b>10.59</b>	<b>7.20</b>
<b>Grit</b>	<b>0.46</b>	<b>0.00</b>
<b>Heels</b>	<b>0.06</b>	<b>0.00</b>
<b>Insulation</b>	<b>8.37</b>	<b>5.00</b>
<b>Resins</b>	<b>0.69</b>	<b>0.00</b>
<b>Pb_gloves</b>	<b>7.21</b>	<b>0.00</b>
<b>Nonconforming</b>	<b>1.52</b>	<b>0.00</b>
<b>SS&amp;C</b>	<b>1.29</b>	<b>6.80</b>
<b>Scrap_metal</b>	<b>33.41</b>	<b>0.00</b>
<b>Sludge</b>	<b>2.76</b>	<b>1.40</b>
<b>Solutions</b>	<b>0.00</b>	<b>0.00</b>
<b>Pu_Fluorides</b>	<b>0.00</b>	<b>0.00</b>

Table C.2 Waste characterization of the LS substreams, wt %

Ash	Crucibles		Chloride salts		Combustibles		Firebrick		Glass	
Pu	0.17	Pu	PuO <sub>2</sub>	0.27	Pu	0.30	Pu	1.36	Pu	0.05
SiO <sub>2</sub>	45.96	PuO <sub>2</sub>	NaCl	23.97	C	18.00	MgO	10.60	SiO <sub>2</sub>	88.95
C	24.00	MgO	MgCl <sub>2</sub>	23.92	H <sub>2</sub> O	5.00	SiO <sub>2</sub>	20.00	Pb	3
Al <sub>2</sub> O <sub>3</sub>	7.00	ZrO	CaCl <sub>2</sub>	24.92	CH <sub>4</sub>	20.00	CaCO <sub>3</sub>	5.00	B	8
CaO	7.00	Al <sub>2</sub> O <sub>3</sub>	KCl	24.92	N <sub>2</sub>	0.70	Al <sub>2</sub> O <sub>3</sub>	52.00	Mg	5
Fe <sub>2</sub> O <sub>3</sub>	7.00	CaCl <sub>2</sub>	Am	0.20	C <sub>6</sub> H <sub>5</sub> Cl	24.00	Am	1.00		
Na <sub>2</sub> O	5.87	NaCl	ZnCl <sub>2</sub>	1.80	SiO <sub>2</sub>	5.00	CaO	10.00		
Pb	2.00	KCl			Al <sub>2</sub> O <sub>3</sub>	7.00				
Cr	1.00	SiO <sub>2</sub>			Fe <sub>2</sub> O <sub>3</sub>	5.00				
					O <sub>2</sub>	10.00				
					S	5.00				
Graphite		Grit	Heels		Insulation		Resins		Pb_gloves	
Pu	0.10	Pu	Pu	1.40	Pu	0.25	Pu	0.12	Pu	0.04
CaF <sub>2</sub>	1.59	SiO <sub>2</sub>	C <sub>3</sub> H <sub>7</sub> O	10.00	Al	50.10	C	30.00	Pb	10
C	96.31	Al <sub>2</sub> O <sub>3</sub>	MgO	23.00	SiO <sub>2</sub>	49.65	H <sub>2</sub>	9.88	C	50
Mg	0.50	MgO	HNO <sub>3</sub>	8.00			Na	60.00	H <sub>2</sub>	5
MgO	0.50		CaO	6.00					O <sub>2</sub>	30
Ca	0.50		Fe <sub>2</sub> O <sub>3</sub>	6.00					N <sub>2</sub>	4.62
CaO	0.50		Al <sub>2</sub> O <sub>3</sub>	7.00					S	0.34
			SiO <sub>2</sub>	18.00						
			NaCl	5.20						
			KCl	5.20						
			C <sub>2</sub> H <sub>6</sub>	5.20						
			C	5.00						

Table C.2 Waste characterization of the LS substreams, wt % (continued)

Scrap_metal	Sludge		Solutions		SS&C		Nonconforming		
Pu	0.05	Pu	0.02	H <sub>2</sub> O	90.00	Pu	0.52	Pu	0.00
Fe	65.00	H <sub>2</sub> O	25.28	HNO <sub>3</sub>	10.00	CaF <sub>2</sub>	8.00	CaCO <sub>3</sub>	10.00
Fe <sub>2</sub> O <sub>3</sub>	25.00	Fe	11.00			MgO	81.48	Fe <sub>2</sub> O <sub>3</sub>	10.00
Cu	2.00	Np	0.10			Ca	5.00	MgO	10.00
Al	7.00	U	0.30					H <sub>2</sub> O	40.00
Al <sub>2</sub> O <sub>3</sub>	0.95	Fe <sub>2</sub> O <sub>3</sub>	10.00					CH <sub>4</sub>	10.00
		SiO <sub>2</sub>	8.00					C	20.00
		MgO	15.00						
		C <sub>3</sub> H <sub>8</sub> O	10.00						
		C <sub>3</sub> H <sub>6</sub>	6.00						
		C	3.00						
		CH <sub>4</sub>	5.00						
		C <sub>2</sub> H <sub>5</sub> Cl	6.30						

Table C.3 Waste characterization of the RS substreams, wt %

Ash	Crucibles	Chloride salts	Graphite	Insulation
Pu	Pu	PuO <sub>2</sub>	Pu	Pu
5.13	1.63	7.90	5.69	4.40
SiO <sub>2</sub>	PuO <sub>2</sub>	NaCl	CaF <sub>2</sub>	Al
45.00	1.00	22.10	1.00	48.00
C	MgO	MgCl <sub>2</sub>	C	SiO <sub>2</sub>
20.00	35.00	22.00	91.31	47.60
Al <sub>2</sub> O <sub>3</sub>	ZrO	CaCl <sub>2</sub>	Ca	
7.00	9.37	22.00	0.50	
CaO	Al <sub>2</sub> O <sub>3</sub>	KCl	Mg	
7.00	30.00	23.00	0.50	
Fe <sub>2</sub> O <sub>3</sub>	CaCl <sub>2</sub>	Am	MgO	
7.00	1.00	1.00	0.50	
Na <sub>2</sub> O	NaCl	ZnCl <sub>2</sub>	CaO	
5.87	1.00	2.00		
Pb	KCl			
2.00	1.00			
Cr	SiO <sub>2</sub>			
1.00	20.00			
Pu_Fluorides	SS&C	Sludge	Solutions	
PuF <sub>4</sub>	Pu	Pu	H <sub>2</sub> O	
97.00	4.80	4.30	90.00	
C <sub>3</sub> H <sub>7</sub> O	CaF <sub>2</sub>	H <sub>2</sub> O	HNO <sub>3</sub>	
3.00	8.00	25.00	10.00	
	MgO	Fe		
	PuF <sub>4</sub>	Np		
	Ca	U		
	Mg	Fe <sub>2</sub> O <sub>3</sub>		
		SiO <sub>2</sub>		
		MgO		
		C <sub>3</sub> H <sub>7</sub> O		
		C <sub>3</sub> H <sub>8</sub>		
		C		
		CH <sub>4</sub>		
		C <sub>6</sub> H <sub>5</sub> Cl		
		5.30		



**Appendix D**

**EFFECT OF TEMPERATURE ON GLASS FORMATION  
FOR LS AND RS WASTE CATEGORIES**



Appendix D presents a series of tables of data about the glass formation using the GMODS process. Every table shows the quantity and composition of the feed material in addition to the quantity and composition of the glass formed.

The information about the different waste stream categories used in this study was obtained from open literature sources on Rocky Flats inventory.<sup>1,2</sup> For some substreams composition information is was necessary to adapt some heuristics and previous experiences with similar waste streams.

The simulation on glass formation considers the production of high-performance glass. The algorithms for glass formation applied to this study assumed performance equivalent to high-level glass. Studies done at Savannah River Laboratory and at Clemson University on high-level glass were incorporated in this simulation.

Table D.1 presents the mass and composition of the feed and glass formed for the different categories of the LS waste material. Table D.2 presents the mass and composition of the feed and glass formed for the different categories of RS waste material. Table D.3 presents the feed and glass formed for the total LS material. It is assumed that every subcategory pertaining to the LS category has been mixed in one stream. Table D.4 presents the feed and glass formed for the total RS material. It is assumed that every subcategory pertaining to the RS category have been mixed together in one stream. Table D.5 presents the feed and glass formed for the combination of LS and RS scrap. This table assumed that every subcategory of both LS and RS scrap categories have been mixed together in one stream. Finally, Table D.6 presents the feed and glass formed for a hypothetical feed of pure  $\text{PuO}_2$ . For simulation purposes it has been assumed that 100 kg/w of  $\text{PuO}_2$  has been fed into the system. The model added enough material to form a glass and to keep the final concentration of  $\text{PuO}_2$  below the critical limit of 10 wt %.

Table D.1. Effect of temperature on glass formation for LS waste categories

Ash(LS)		Glass Ash(LS)			Chloride(LS)			Glass Chlorides			
Temp, Celcius	1050.00	1050	1060.00	Temp, Celcius	1103.00	1122.00	1167.00	Temp, Celcius	1103.00	1122.00	1167.00
Glass mass, kg	1.42	1.42	1.27	Glass mass, kg	6.43	4.76	3.07	Glass mass, kg	6.43	4.76	3.07
Vol, ft (sp gr 1.5)	0.47	0.47	0.42	Vol, ft (sp gr 1.5)	2.14	1.59	1.02	Vol, ft (sp gr 3)	2.14	1.59	1.02
Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %
Pu	0.17	0.12	0.13	PuO <sub>2</sub>	0.27	0.06	0.09	PuO <sub>2</sub>	0.04	0.06	0.09
SiO <sub>2</sub>	45.96	49.81	48.21	NaCl	23.97	0.65	1.00	NaCl	0.48	0.65	1.00
C	24.00			MgCl <sub>2</sub>	23.92	0.65	1.00	MgCl <sub>2</sub>	0.48	0.65	1.00
Al <sub>2</sub> O <sub>3</sub>	7.00	4.94	5.48	CaCl <sub>2</sub>	24.92	0.68	1.04	CaCl <sub>2</sub>	0.50	0.68	1.04
CaO	7.00	4.94	5.49	KCl	24.92	0.68	1.04	KCl	0.50	0.68	1.04
Fe <sub>2</sub> O <sub>3</sub>	7.00	4.94	5.49	Am	0.20	0.04	0.06	Am <sub>2</sub> O <sub>3</sub>	0.03	0.04	0.06
Na <sub>2</sub> O	5.87	14.91	12.58	ZnCl <sub>2</sub>	1.80	0.38	0.59	ZnCl <sub>2</sub>	0.28	0.38	0.59
Pb	2.00	0.00	0.00	SiO <sub>2</sub>	59.12	59.12	59.12	SiO <sub>2</sub>	59.12	59.12	59.12
Cr	1.00	0.71	0.78	B <sub>2</sub> O <sub>3</sub>	14.27	14.27	14.27	B <sub>2</sub> O <sub>3</sub>	14.27	14.27	14.27
		19.64	21.83	Na <sub>2</sub> O	19.09	16.43	10.87	Na <sub>2</sub> O	19.09	16.43	10.87
				PbO	0.00	0.00	0.00	PbO	0.00	0.00	0.00
				CaO	1.71	2.31	3.57	CaO	1.71	2.31	3.57
				MgO	1.37	1.86	2.87	MgO	1.37	1.86	2.87
				K <sub>2</sub> O	2.13	2.87	4.46	K <sub>2</sub> O	2.13	2.87	4.46

Combustibles(LS)		Glass Combustibles			Graphite(LS)			Glass from Graphite			
Temp, Celcius	1111.00	1135.00	1216.00	Temp, Celcius	1101.00	1122.00	1167.00	Temp, Celcius	1101.00	1122.00	1167.00
Glass mass, kg	0.57	0.42	0.27	Glass mass, kg	0.40	0.30	0.19	Glass mass, kg	0.40	0.30	0.19
Vol, ft (sp gr 1.5)	0.19			Vol, ft (sp gr 1.5)	0.13	0.10	0.06	Vol, ft (sp gr 3)	0.13	0.10	0.06
Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %	Conc. wt %
Pu	0.30	0.70	1.08	Pu	0.10	0.33	0.51	PuO <sub>2</sub>	0.24	0.33	0.51
C	18.00	0.00	0.00	CaF <sub>2</sub>	1.59	0.69	1.07	CaF <sub>2</sub>	0.51	0.69	1.07
H <sub>2</sub> O	5.00			C	96.31	0.00		C	0.00		



Table D.1. Effect of temperature on glass formation for LS waste categories (continued)

Resin(LS)		Glass Resins(LS)			Sludge(LS)		Glass Sludge(LS)		
Temp, Celcius	1178.00	1231	1358.00	Temp, Celcius	1062.00	1086.00	1144.00	Temp, Celcius	1086.00
Massflow, kg	0.01	0	0.01	Massflow, kg	1.00	3.43	2.18	Massflow, kg	4.71
Vol, R (sp gr 1.5)	0.00	0.00	0.00	Vol, R (sp gr 1.5)	0.67	1.57		Vol, R (sp gr 3)	1.57
Conc. wt %				Conc. wt %				Conc. wt %	
Pu	0.12	9.24	13	19.34	Pu	0.02	0.01	PuO <sub>2</sub>	0.00
C	30.00	0.00	0	0.00	H <sub>2</sub> O	25.28	0.42	Fe	0.31
H <sub>2</sub>	9.88				Fe	11.00	0.09	U	0.06
Na	60.00				Np	0.10	2.92	Fe <sub>2</sub> O <sub>3</sub>	2.12
					U	0.30	59.12	SiO <sub>2</sub>	59.12
					Fe <sub>2</sub> O <sub>3</sub>	10.00	4.37	MgO	3.18
					SiO <sub>2</sub>	8.00	0.00	C	0.00
					MgO	15.00	14.27	B <sub>2</sub> O <sub>3</sub>	14.27
					C <sub>2</sub> H <sub>4</sub> O	10.00	18.12	Na <sub>2</sub> O	18.12
					C <sub>2</sub> H <sub>4</sub>	6.00	2.80	Fe <sub>2</sub> O <sub>4</sub>	2.80
					C	3.00			
					CH <sub>4</sub>	5.00			
					C <sub>2</sub> H <sub>2</sub> Cl	6.30			

Scrap Metal(LS)		Glass Scrap Met			Crucible(LS)		Glass Crucibles		
Temp, Celcius	1163.00	1210.00	1328.00	Temp, Celcius	1081.00	1094	1126.00	Temp, Celcius	1094
Massflow, kg	12.40	9.16	5.92	Massflow, kg	1.00	3.91	2.53	Massflow, kg	5.29
Vol, R (sp gr 1.5)	4.13			Vol, R (sp gr 1.5)	0.67	1.30	0.84	Vol, R (sp gr 3)	1.76
Conc. wt %				Conc. wt %				Conc. wt %	
Pu	0.05	0.00	0.01	Pu	0.06	0.028	0.04	PuO <sub>2</sub>	0.02
Fe	65.00	0.69	0.93	PuO <sub>2</sub>	0.05	7.00	14.65	MgO	7.00











Table D.3. Total LS			
Total LS feed		LS glass formation	
Mass flow rate	225,495.00	Mass flow rate	559,350.00
Component	Wt %	Component	Wt %
Pu	0.20	SiO <sub>2</sub>	52.94
SiO <sub>2</sub>	18.00	B <sub>2</sub> O <sub>3</sub>	14.27
C	17.00	Na <sub>2</sub> O	7.47
Al <sub>2</sub> O <sub>3</sub>	4.61	C	0.00
CaO	0.86	Al <sub>2</sub> O <sub>3</sub>	6.18
Fe <sub>2</sub> O <sub>3</sub>	9.48	CaO	0.70
Na <sub>2</sub> O	0.19	Fe <sub>2</sub> O <sub>3</sub>	3.82
Pb	1.12	Cr	0.01
Cr	0.03	PuO <sub>2</sub>	0.07
PuO <sub>2</sub>	0.01	MgO	1.29
MgO	2.78	ZrO	0.05
ZrO	0.11	CaCl <sub>2</sub>	0.04
CaCl <sub>2</sub>	0.72	NaCl	0.04
NaCl	0.70	KCl	0.04
KCl	0.72	MgCl <sub>2</sub>	0.04
MgCl <sub>2</sub>	0.70	ZnCl <sub>2</sub>	0.02
Am	0.06	B	0.36
ZnCl <sub>2</sub>	0.05	CaF <sub>2</sub>	0.01
H <sub>2</sub> O	1.78	Mg	0.01
CH <sub>4</sub>	2.17	Ca	0.01

Table D.3. Total LS (continued)			
Total LS feed		LS glass formation	
Mass flow rate	225,495.00	Mass flow rate	559,350.00
N <sub>2</sub>	0.40	Al	0.35
C <sub>6</sub> H <sub>5</sub> Cl	2.40	Fe	1.17
O <sub>2</sub>	3.10	Cu	0.27
S	0.50	U	0.00
CaCO <sub>3</sub>	0.40	Fe <sub>3</sub> O <sub>4</sub>	10.66
B	0.90	K <sub>2</sub> O	0.16
CaF <sub>2</sub>	0.27	Am <sub>2</sub> O <sub>3</sub>	0.02
Mg	0.12		
Ca	0.12		
C <sub>3</sub> H <sub>7</sub> O	0.30		
HNO <sub>3</sub>	0.00		
C <sub>3</sub> H <sub>8</sub>	0.17		
Al	6.53		
H <sub>2</sub>	0.43		
Na	0.41		
Cu	0.67		
Np	0.00		
U	0.01		
Fe	22.02		

Table D.4. Total RS			
RS feed		RS glass formation	
Mass flow rate kg/w	42,997.00	Mass flow rate kg/w	93,105.00
Component	Wt %	Component	Wt %
Pu	3.34	SiO <sub>2</sub>	55.31
SiO <sub>2</sub>	23.11	B <sub>2</sub> O <sub>3</sub>	14.27
C	15.40	Na <sub>2</sub> O	9.95
Al <sub>2</sub> O <sub>3</sub>	4.31	C	0.00
CaO	3.12	Al <sub>2</sub> O <sub>3</sub>	3.81
Fe <sub>2</sub> O <sub>3</sub>	3.22	CaO	3.17
Na <sub>2</sub> O	2.58	Fe <sub>2</sub> O <sub>3</sub>	1.49
Pb	0.88	Cr	0.20
Cr	0.44	PuO <sub>2</sub>	2.70
PuO <sub>2</sub>	2.53	MgO	4.65
MgO	7.17	ZrO	0.18
ZrO	0.38	CaCl <sub>2</sub>	0.41
CaCl <sub>2</sub>	6.97	NaCl	0.42
NaCl	7.00	KCl	0.43
KCl	7.29	MgCl <sub>2</sub>	0.41
MgCl <sub>2</sub>	6.90	ZnCl <sub>2</sub>	0.29
Am	0.32	CaF <sub>2</sub>	0.04
ZnCl <sub>2</sub>	0.63	Ca	0.01
CaF <sub>2</sub>	0.62	Mg	0.01
Ca	0.24	Al	0.15

Table D.4. Total RS (continued)			
RS feed		RS glass formation	
Mass flow rate kg/w	42,997.00	Mass flow rate kg/w	93,105.00
Mg	0.24	Fe	0.01
Al	2.40	U	0.00
PuF <sub>4</sub>	0.03	Fe <sub>3</sub> O <sub>4</sub>	0.08
H <sub>2</sub> O	0.35	K <sub>2</sub> O	1.85
Fe	0.14	Am <sub>2</sub> O <sub>3</sub>	0.14
Np	0.00		
U	0.00		
C-3H <sub>7</sub> O	0.14		
C <sub>3</sub> H <sub>8</sub>	0.07		
CH <sub>4</sub>	0.07		
C <sub>6</sub> H <sub>5</sub> Cl	0.07		

<b>Table D.5. Total scrap including LS and RS scrap</b>			
<b>Total scrap feed</b>		<b>Total scrap glass formation</b>	
<b>Mass flow rate, kg/w</b>	<b>268,492.00</b>	<b>Mass flow rate, kg/w</b>	<b>6524,70.</b>
<b>Component</b>	<b>Wt %</b>	<b>Component</b>	<b>Wt %</b>
Pu	0.69	SiO <sub>2</sub>	53.
SiO <sub>2</sub>	18.87	B <sub>2</sub> O <sub>3</sub>	14.
C	16.63	Na <sub>2</sub> O	8.
Al <sub>2</sub> O <sub>3</sub>	4.56	Al <sub>2</sub> O <sub>3</sub>	6.
CaO	1.22	CaO	1.
Fe <sub>2</sub> O <sub>3</sub>	8.48	Fe <sub>2</sub> O <sub>3</sub>	3.
Na <sub>2</sub> O	0.57	Cr	0.
Pb	1.08	PuO <sub>2</sub>	0.
Cr	0.10	MgO	2.
PuO <sub>2</sub>	0.41	ZrO	0.
MgO	3.48	CaCl <sub>2</sub>	0.
ZrO	0.16	NaCl	0.
CaCl <sub>2</sub>	1.72	KCl	0.
NaCl	1.71	MgCl <sub>2</sub>	0.
KCl	1.78	ZnCl <sub>2</sub>	0.
MgCl <sub>2</sub>	1.68	CaF <sub>2</sub>	0.
Am	0.10	Ca	0.
ZnCl <sub>2</sub>	0.14	Mg	0.
CaF <sub>2</sub>	0.33	Al	0.
Ca	0.14	Fe	1.
Mg	0.14	U	0.00
Al	5.87	B	0.

Table D.5. Total scrap including LS and RS scrap (continued)			
Total scrap feed		Total scrap glass formation	
Mass flow rate, kg/w	268,492.00	Mass flow rate, kg/w	6524,70.
Component	Wt %	Component	Wt %
PuF <sub>4</sub>	0.01	Cu	0.
H <sub>2</sub> O	1.55	PbO	0.00
Fe	18.52	Fe <sub>3</sub> O <sub>4</sub>	9.
Np	0.00	K <sub>2</sub> O	0.
U	0.01	Am <sub>2</sub> O <sub>3</sub>	0.
C <sub>3</sub> H <sub>7</sub> O	0.26		
C <sub>3</sub> H <sub>8</sub>	0.15		
CH <sub>4</sub>	1.84		
C <sub>6</sub> H <sub>5</sub> Cl	2.05		
N <sub>2</sub>	0.34		
O <sub>2</sub>	2.61		
S	0.42		
CaCO <sub>3</sub>	0.37		
B	0.75		
HNO <sub>3</sub>	0.00		
H <sub>2</sub>	0.36		
Na	0.35		
Cu	0.56		

<b>Table D.6. Pure PuO<sub>2</sub></b>			
<b>Pure PuO<sub>2</sub> feed</b>		<b>Glass formation from pure PuO<sub>2</sub></b>	
Mass flow rate, kg/w	100.00	Mass flow rate, kg/w	997.69
Component	Wt. %	Component	Wt. %
PuO <sub>2</sub>	100.00	SiO <sub>2</sub>	59.12
		B <sub>2</sub> O <sub>3</sub>	14.27
		Na <sub>2</sub> O	16.58
		PuO <sub>2</sub>	10.02

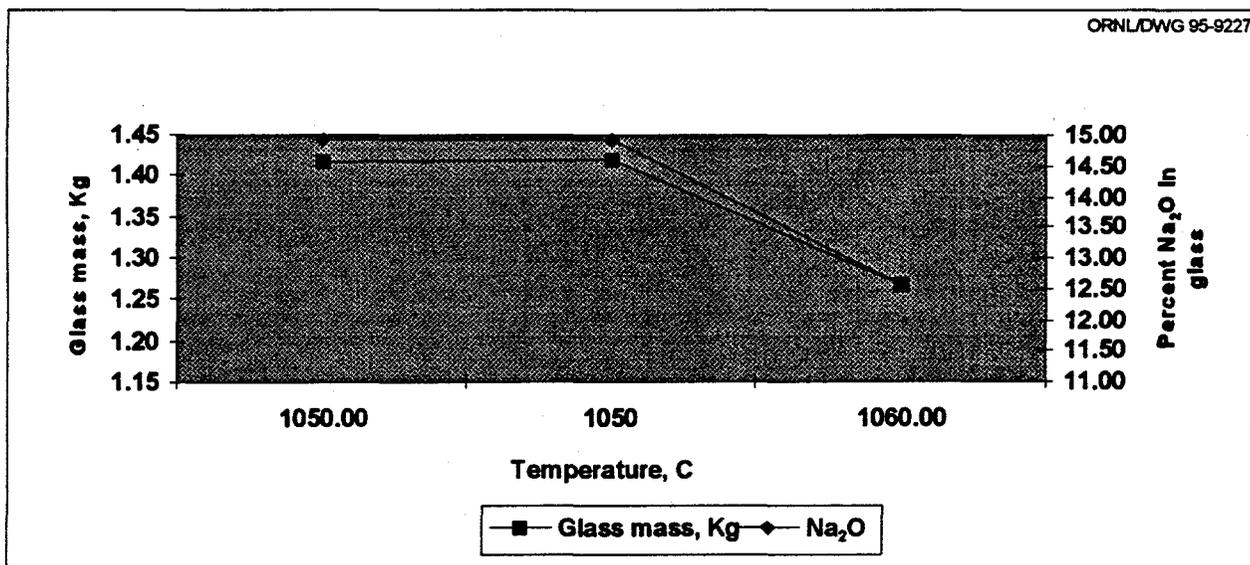


Fig. D.1. Effect of temperature on glass formation for LS—ash.

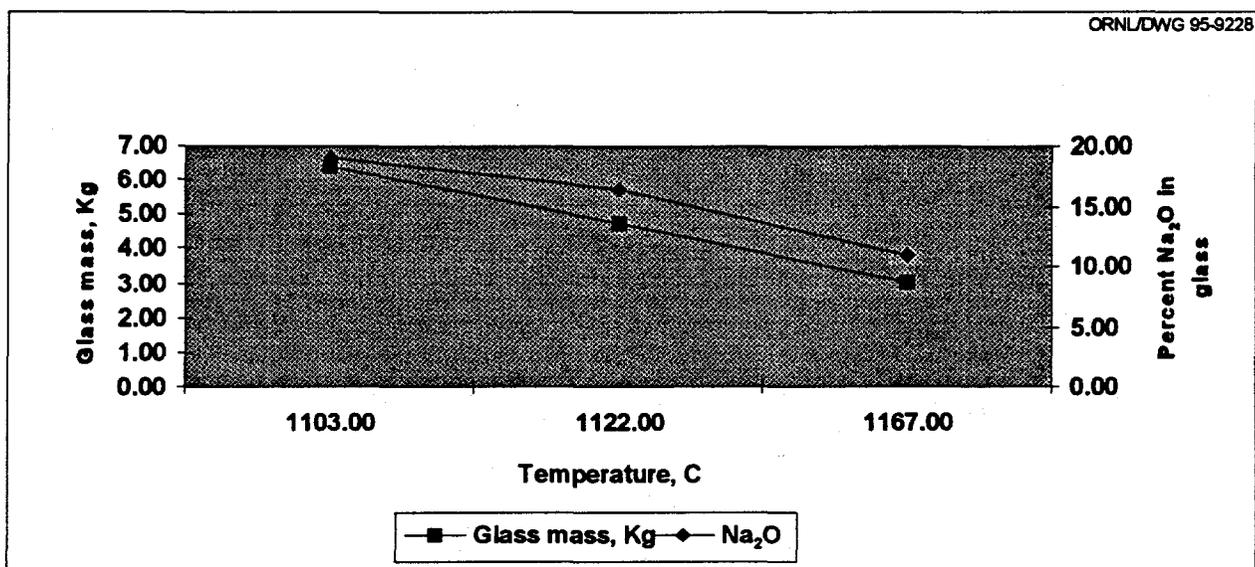


Fig. D.2. Effect of temperature on glass formation for LS—chloride salts.

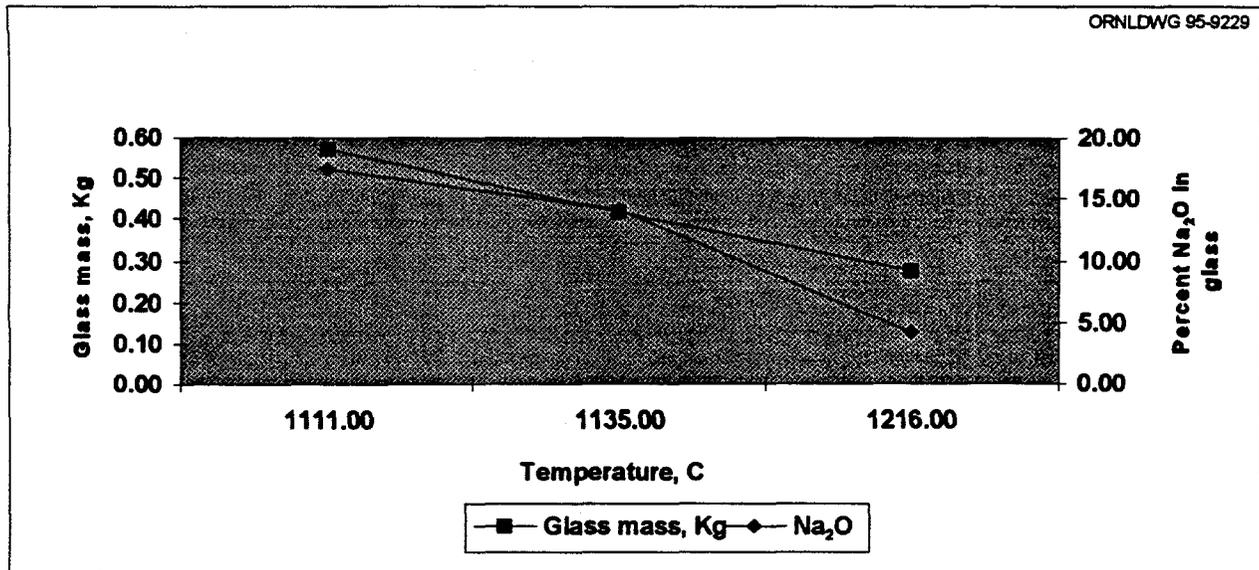


Fig. D.3. Effect of temperature on glass formation for LS—combustibles.

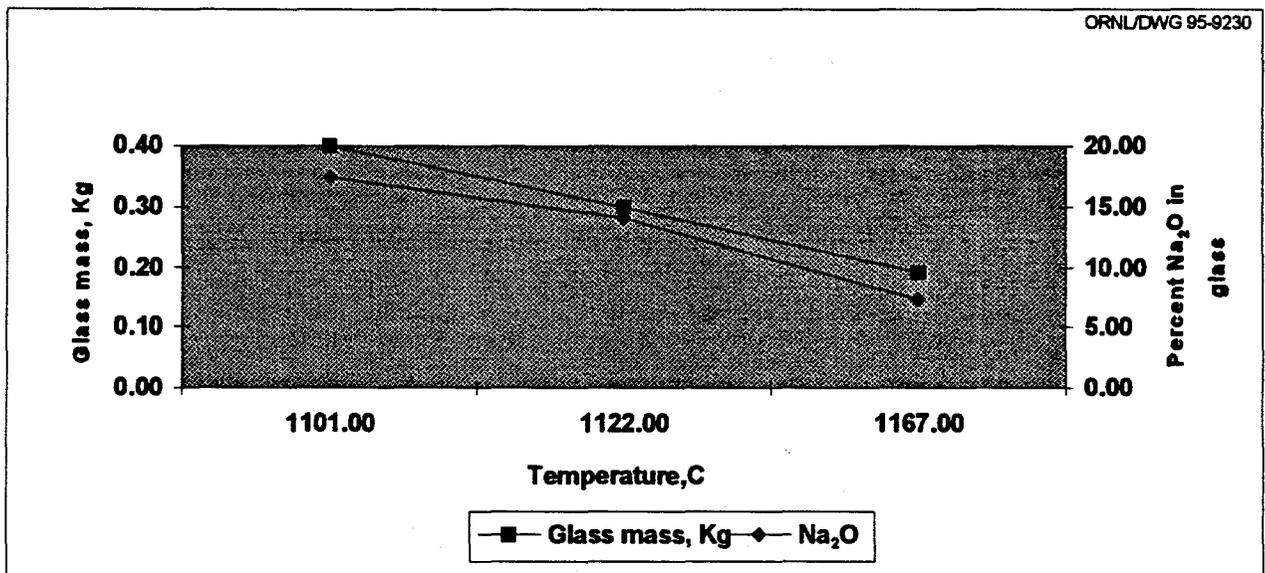


Fig. D.4. Effect of temperature on glass formation for LS—graphite.

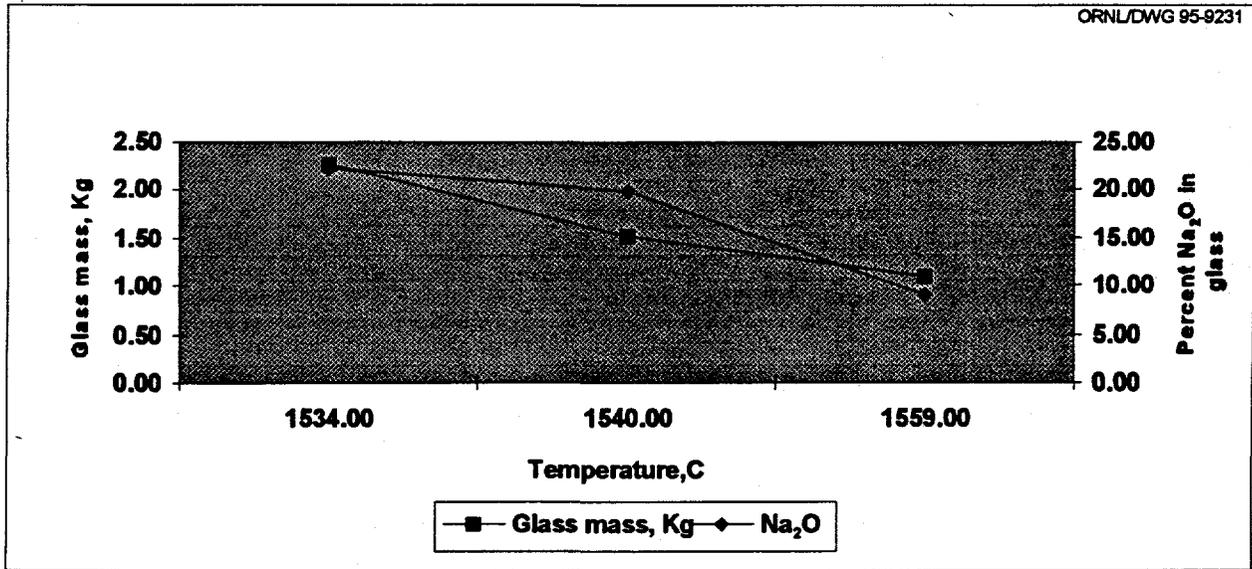


Fig. D.5. Effect of temperature on glass formation for LS—grit.

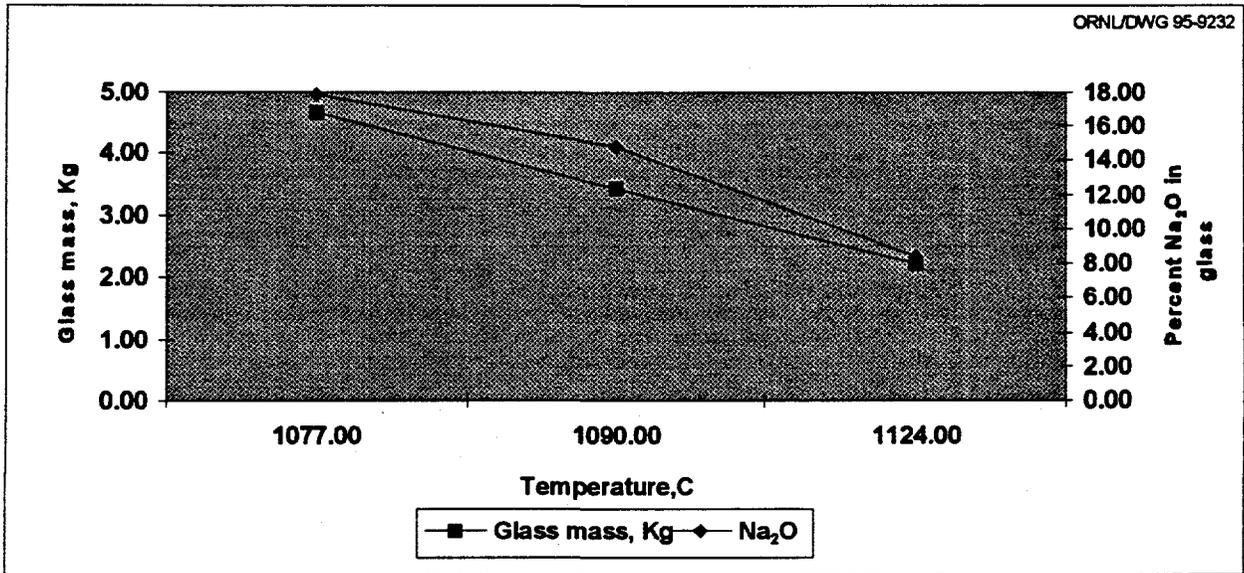


Fig. D.6. Effect of temperature on glass formation for LS—heels.

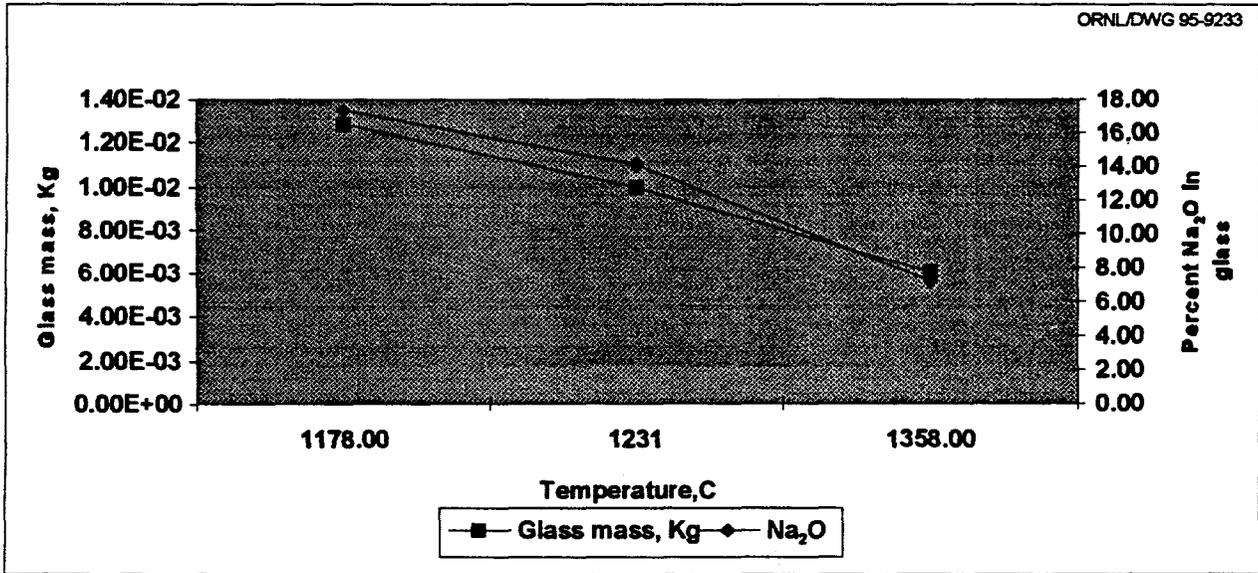


Fig. D.7. Effect of temperature on glass formation for LS—resins.

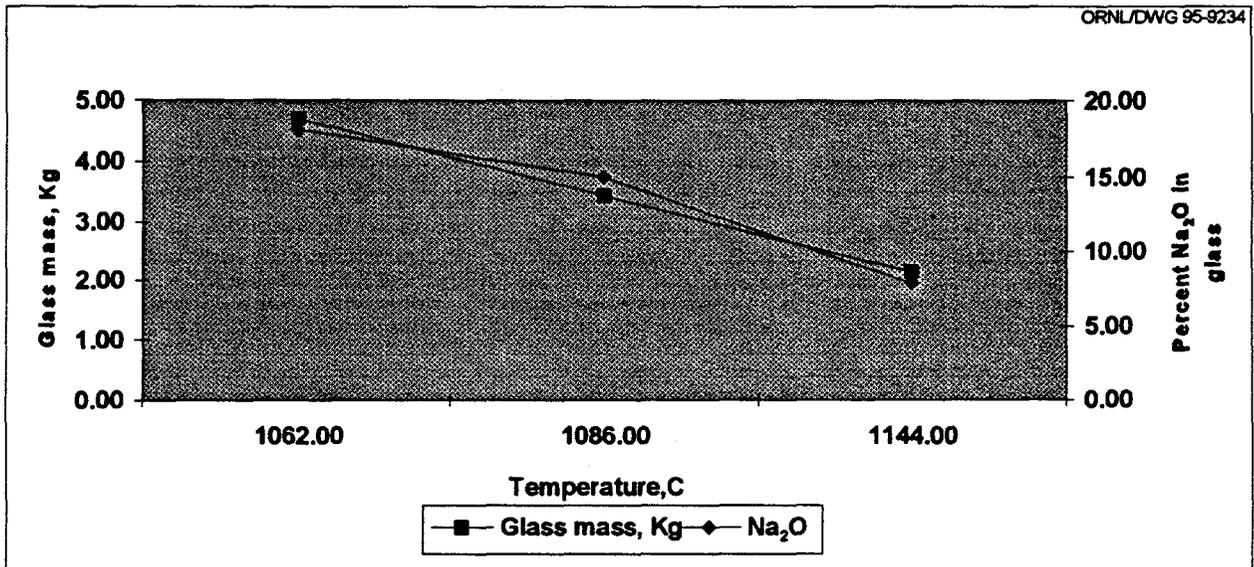


Fig. D.8. Effect of temperature on glass formation for LS—sludges.

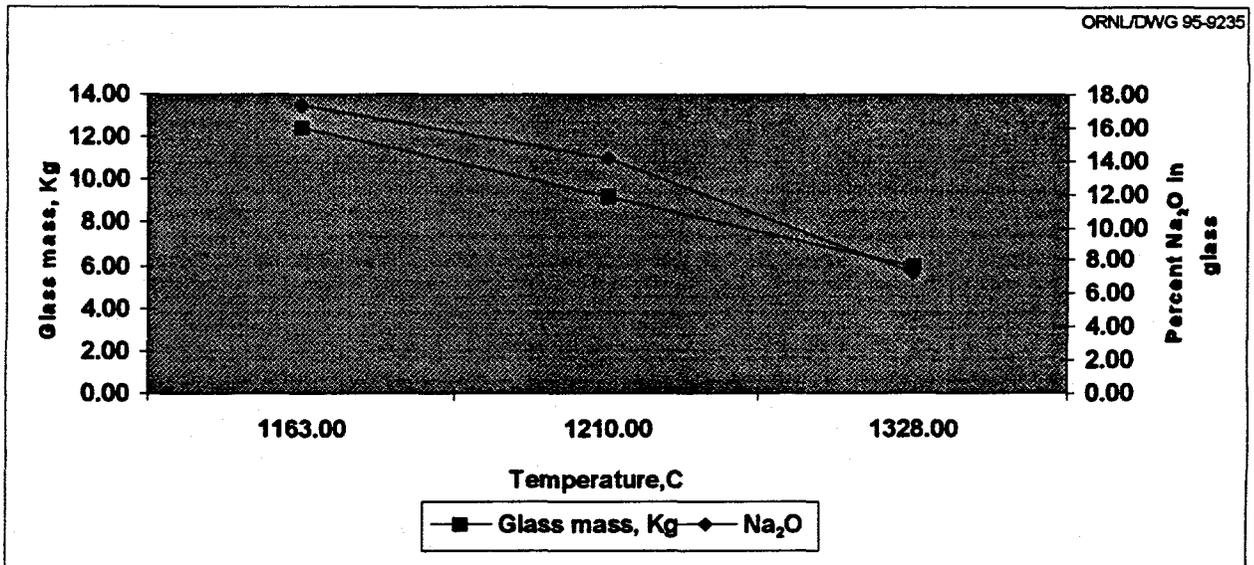


Fig. D.9. Effect of temperature on glass formation for LS—scrap metal.

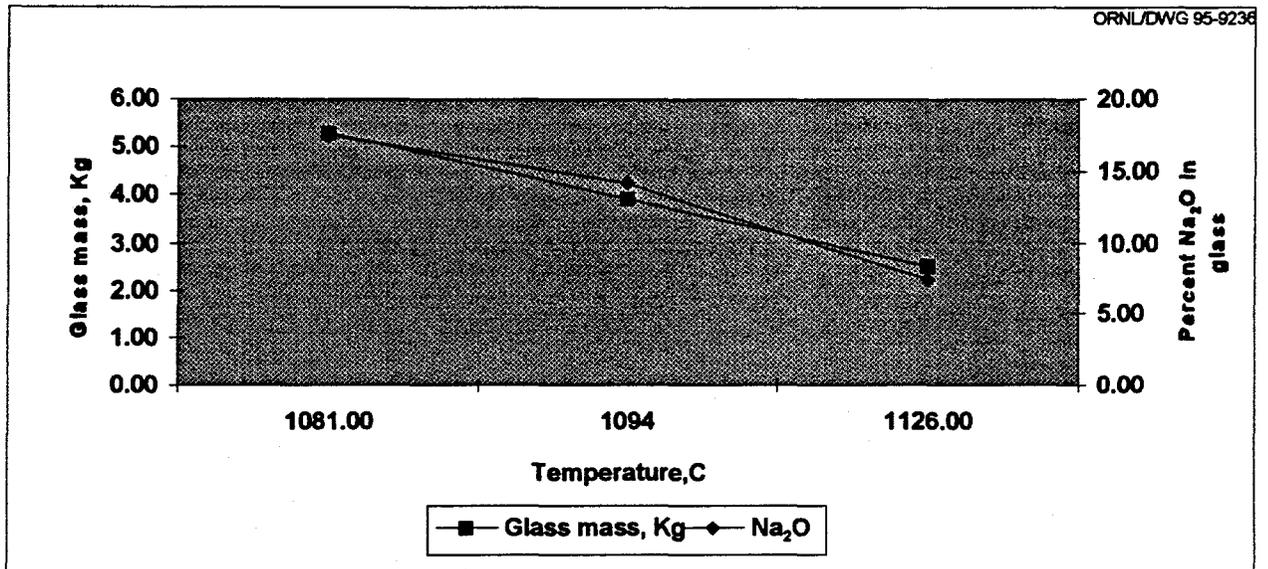


Fig. D.10. Effect of temperature on glass formation for LS—crucibles.

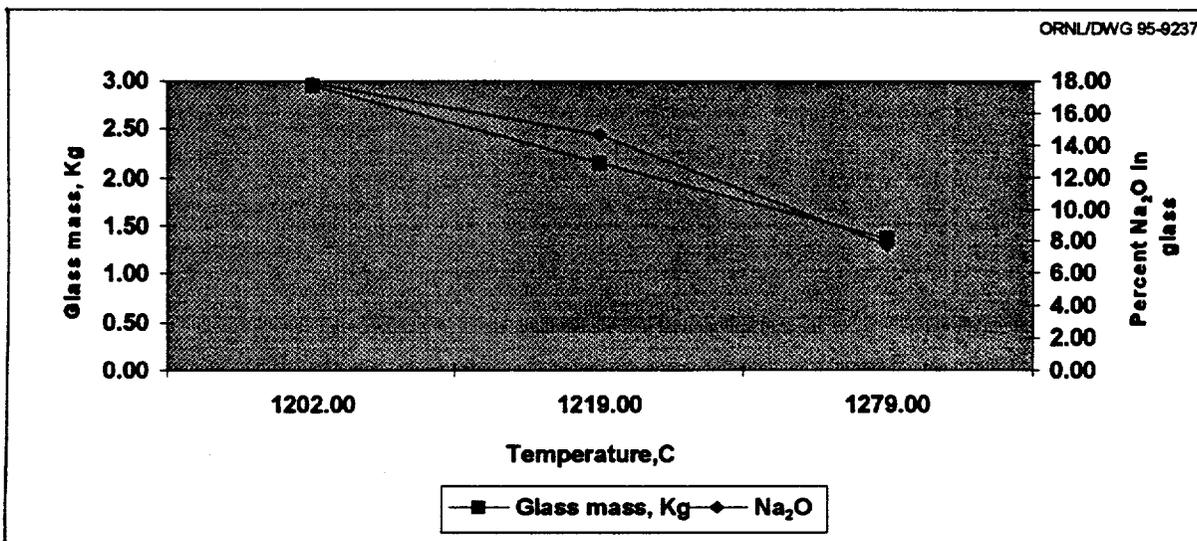


Fig. D.11. Effect of temperature glass formation for LS—firebrick.

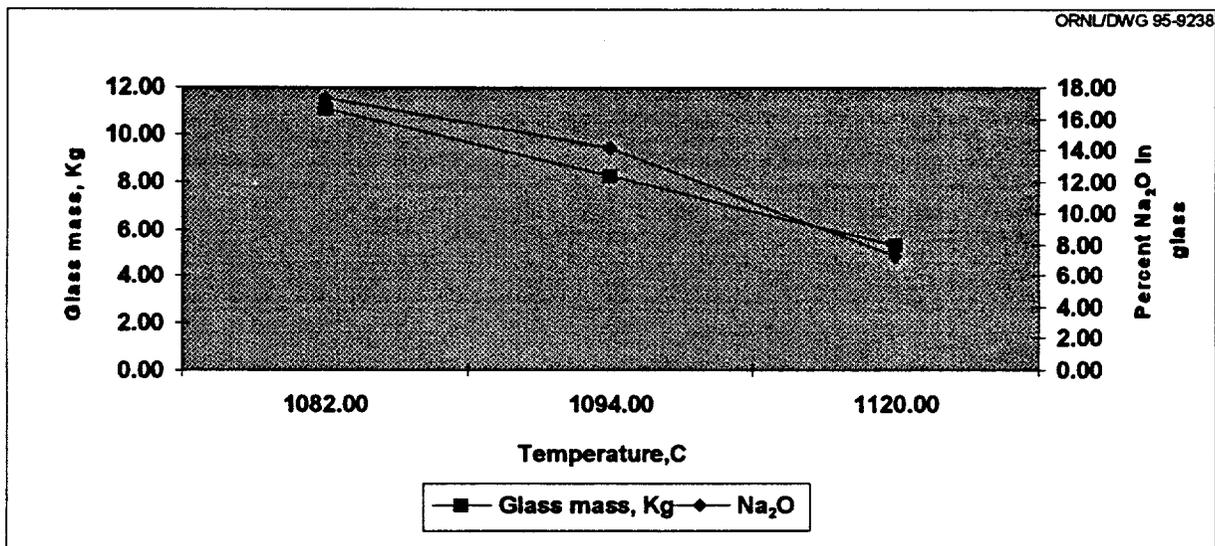


Fig. D.12. Effect of temperature on glass formation for LS—SS&C.

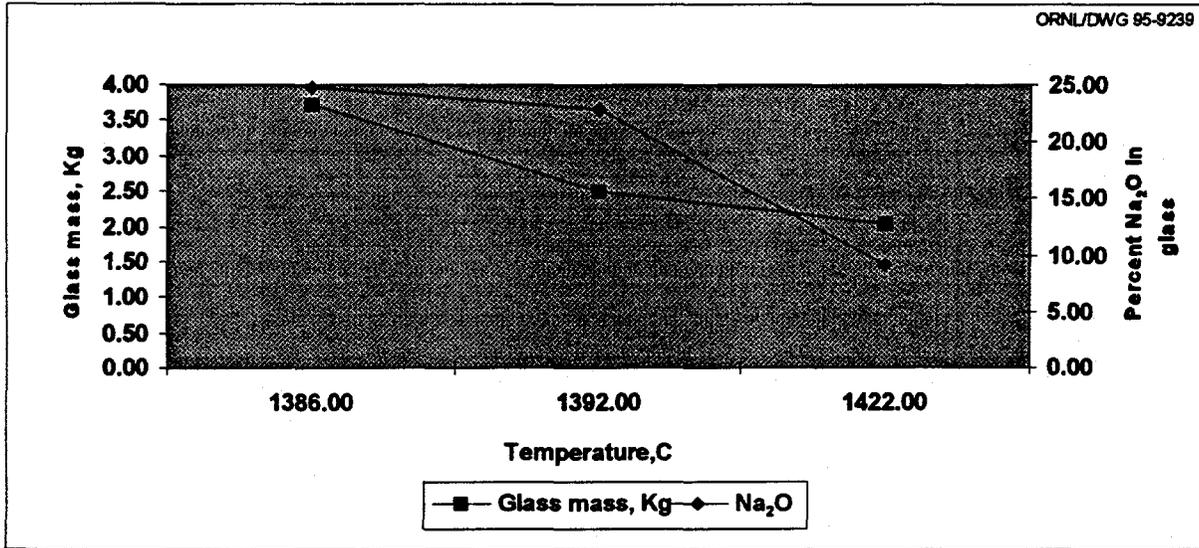


Fig. D.13. Effect of temperature on glass formation for LS—insulation.

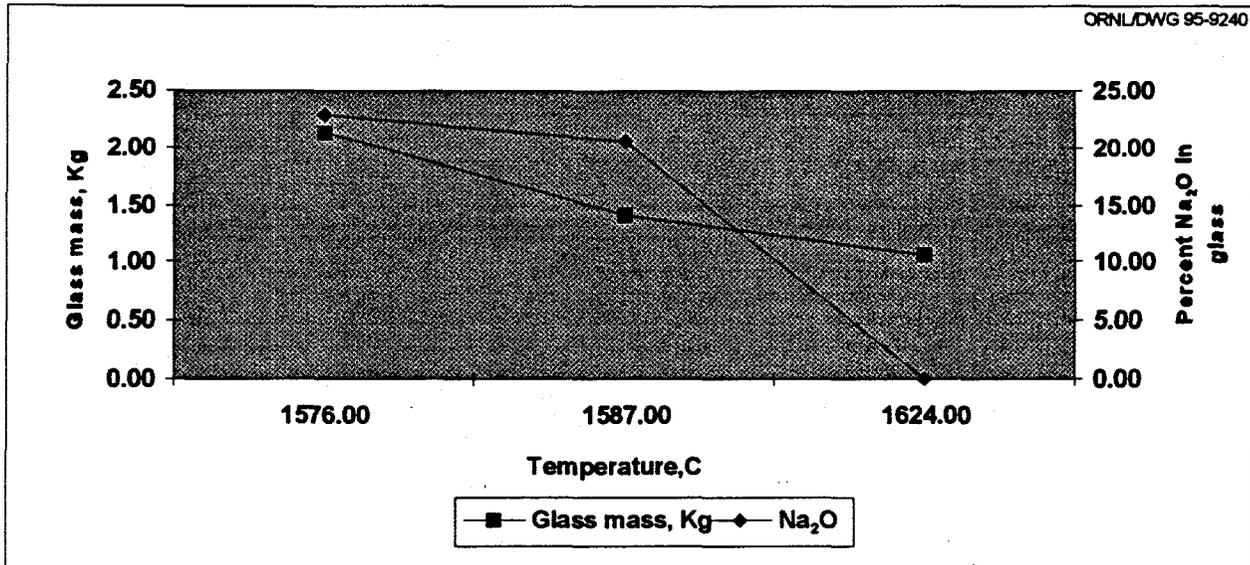


Fig. D.14. Effect of temperature on glass formation for LS—glass.

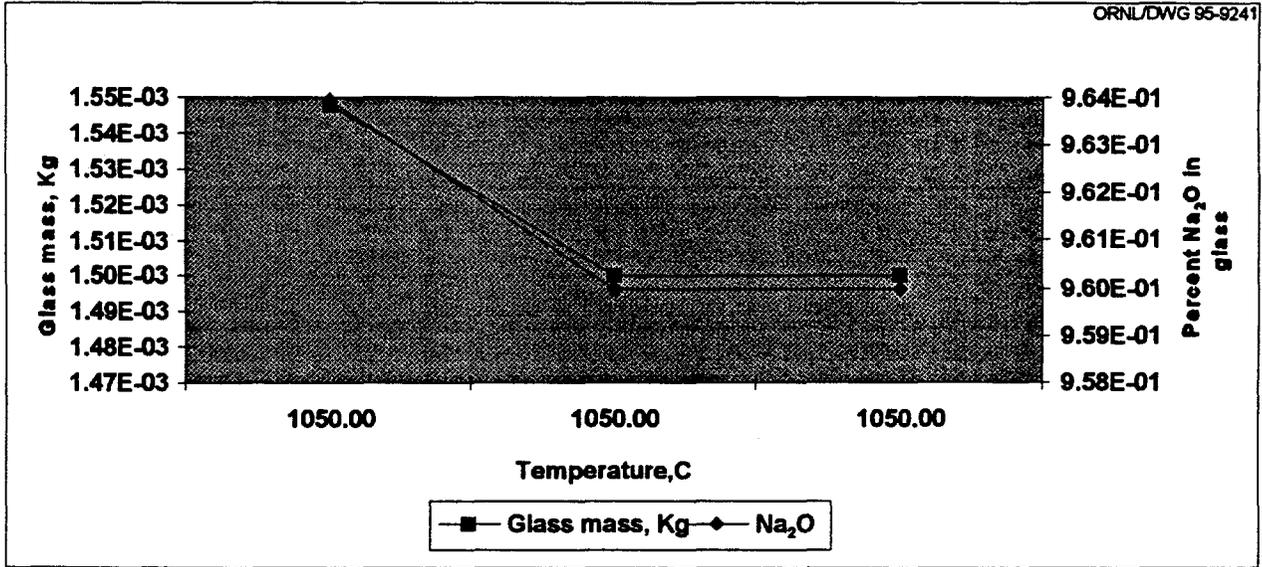


Fig. D.15. Effect of temperature on glass formation for LS—lead gloves.

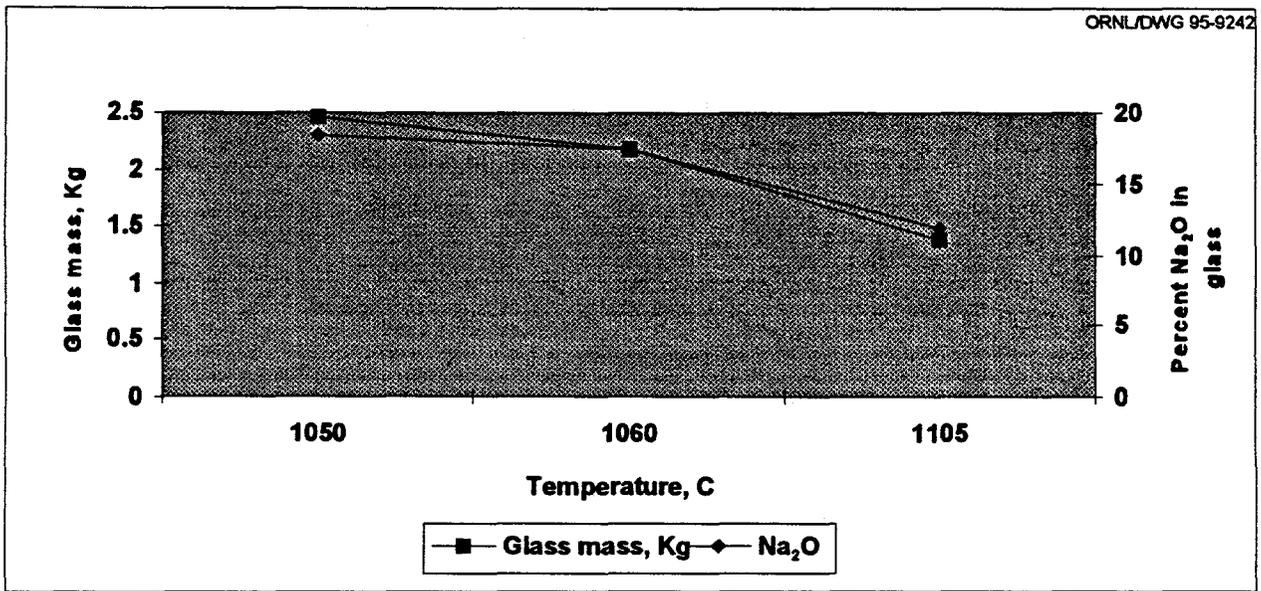


Fig. D.16. Effect of temperature on glass formation for RS—ash.

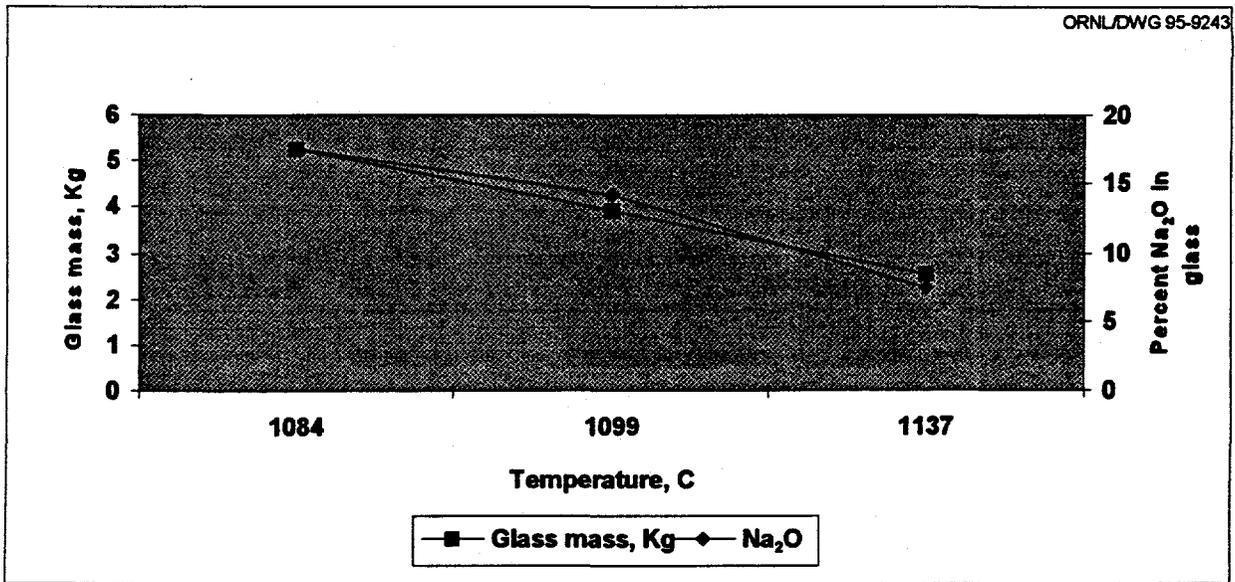


Fig. D.17. Effect of temperature on glass formation for RS—crucibles.

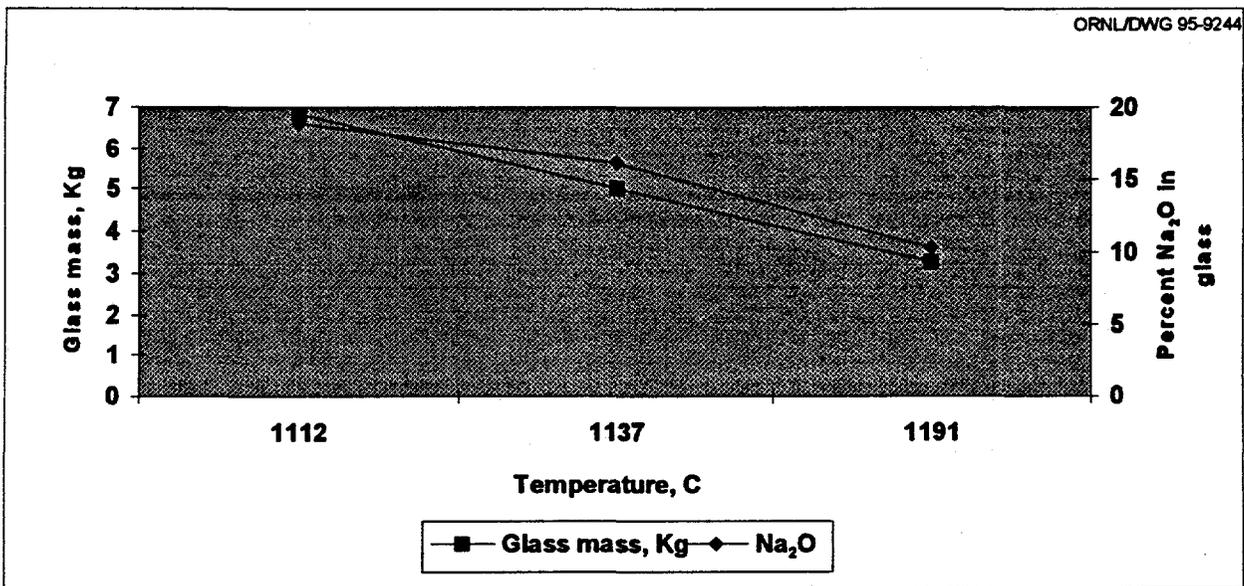


Fig. D.18. Effect of temperature on glass formation for RS—chloride salts.

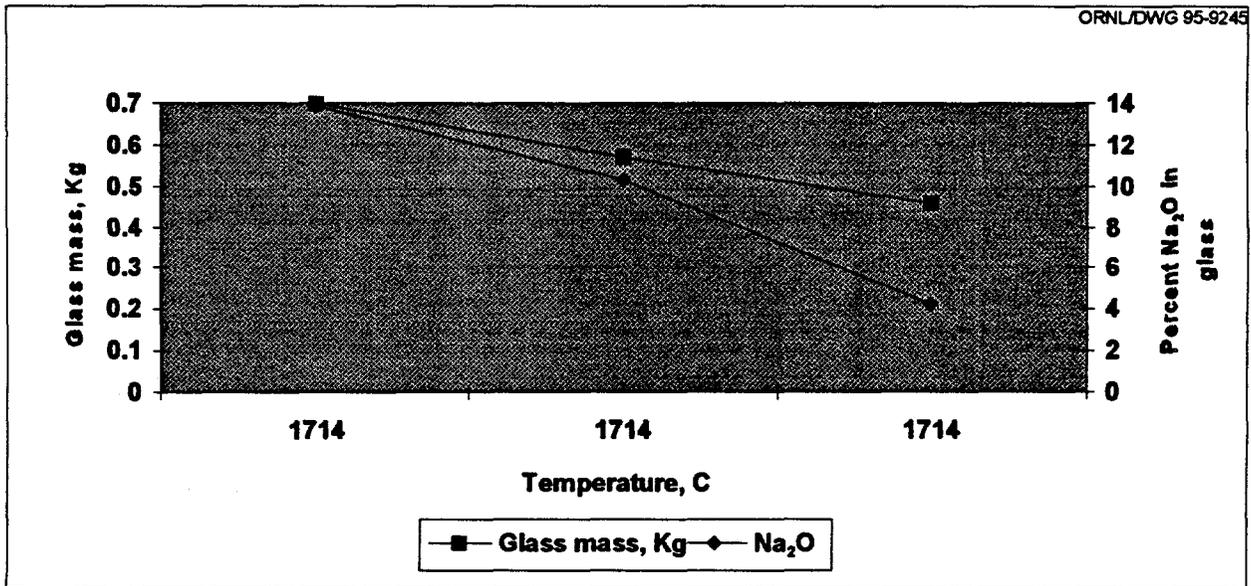


Fig. D.19. Effect of temperature on glass formation for RS—graphite.

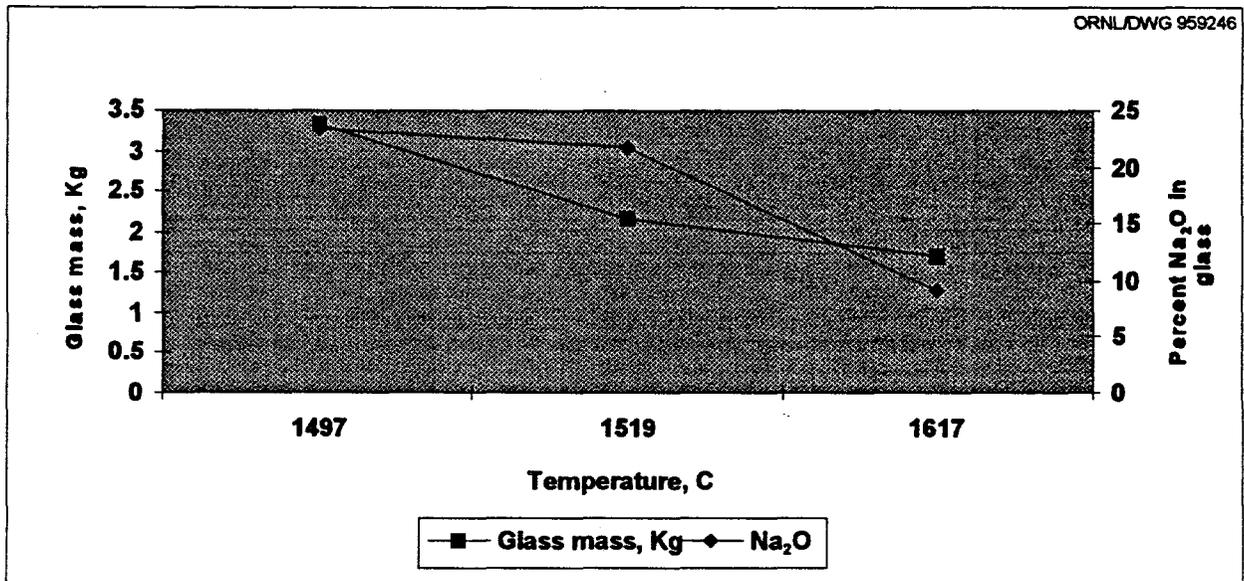


Fig. D.20. Effect of temperature on glass formation for RS—insulation.

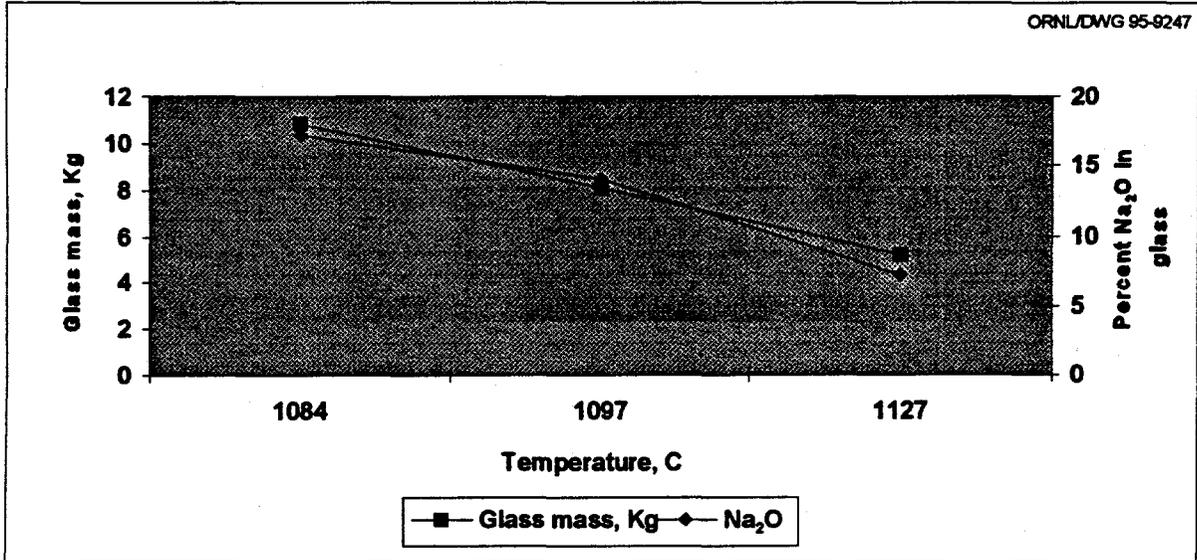


Fig. D.21. Effect of temperature on glass formation for RS—SS&C.

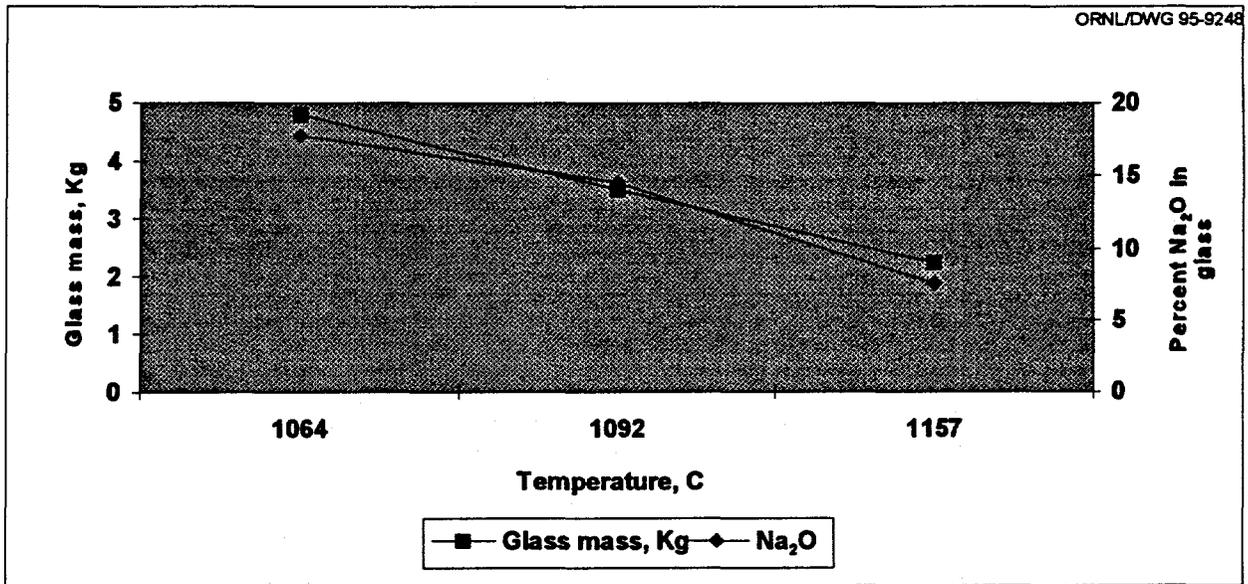


Fig. D.22. Effect of temperature on glass formation for RS—sludge.

**D.1. REFERENCES FOR APPENDIX D.**

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2. Surplus Fissile Material Control and Disposition Program, *Pretreatment Process for Immobilization Initial Report*, L-18802-111, PreDecisional Draft, February 27, 1995.

**Appendix E**  
**FEATURES OF FLOW**



## **E.1 GENERAL FEATURES OF FLOW**

FLOW simulates the chemical and physical interactions involved in waste management operations and processes these operations simultaneously on several levels. FLOW has several desirable attributes:

- **user friendly**—Users create FLOWsheets, supply data, and control simulations using intuitive graphical objects, menus, and pop-up dialog boxes.
- **graphical interface**—Icons representing unit operations, inputs, and outputs are selected, placed on the working FLOWsheet, and connected with a mouse.
- **general command menu**—The command menu gives the user control of many features of the simulation package.
- **C++ language**—FLOW's design emphasizes modularity and object-oriented programming concepts.
- **pop-up dialog boxes**—Dialog boxes prompt the user for necessary input.

## **E.2 CHARACTERISTICS AND FEATURES USEFUL FOR THE GMODS PROCESS STUDY**

A number of characteristics and features make FLOW a good choice for the GMODS process study:

- FLOWsheets can be constructed quickly and easily without extensive user training;
- Simulations run quickly because built-in process heuristics replace time-consuming thermodynamic calculations;
- Multiple cases can be run in a short time;
- FLOW can be run on any DOS- or WINDOWS-based PC with a coprocessor, and, because it was developed by ORNL, no licensing fee must be paid by DOE or its contractors;
- Cost, risk, and uncertainty models are built in and can be integrated directly into performance simulations;
- Components can be represented in a variety of ways—chemical formulas, chemical and trade names, physical descriptions;

- Heuristic handling of component properties and behavior permits streamlined specification of separations and realistic results even when data are missing;
- Decision modules permit integration of acceptance criteria, operating constraints, blend recipes, and regulatory and other requirements in the flowsheet;
- User unit operation models can be programmed and compiled independent of FLOW in several languages;
- Users can easily design, code, compile, and incorporate their own models;
- Multilevel FLOWsheet capabilities allow top-level systems models (e.g., the national waste system, sites, or facilities) and detailed process model simulations to be integrated;
- Models can be built from (a) the top down or from (b) the bottom up;
- Users can build sophisticated models of process technologies from the basic modules that FLOW provides; and,
- FLOW has been compiled using a DOS extender, allowing large problems to be run.

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