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Demonstration of an Approach to Waste Form Qualification Through Simulation of Liquid-Fed Ceramic Melter Process Operations

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SUMMARY

During fiscal year 1982, the U.S. Department of Energy (DOE) assigned responsibility for managing civilian nuclear waste treatment programs in the United States to the Nuclear Waste Treatment Program (NWTP) at the Pacific Northwest Laboratory (PNL). One of the principal objectives of this program is to establish relationships between vitrification process control and glass quality. Users of the liquid-fed ceramic melter (LFCM) process will need such relationships in order to establish acceptance of vitrified high-level nuclear waste at a licensed federal repository without resorting to destructive examination of the canisters. The objective is to be able to supply a regulatory agency with an estimate of the composition, durability, and integrity of the glass in each waste glass canister produced from an LFCM process simply by examining the process data collected during the operation of the LFCM. The work described here will continue through FY-1987 and culminate in a final report on the ability to control and monitor an LFCM process through sampling and process control charting of the LFCM feed system.

The NWTP is demonstrating an approach to qualification of vitrified high-level waste forms through the simulation of a hypothetical LFCM process. The approach addresses the prediction of glass composition, which is the most important determinant of glass quality. This is conceptually very simple, amounting to a mass balance that mathematically states, "what goes in comes out." For institutional reasons, however, there is a need to understand the uncertainty and the reasons for the uncertainty in the composition of the glass (see Section 1.1). The two major concerns are: What fluctuations in glass composition can be expected from an LFCM process? How will these fluctuations affect the quality of the glass? The estimate of durability should be given in terms of a most likely value with upper and lower confidence limits.

The composition of the glass from an LFCM process will fluctuate randomly about the intended (target) composition because of errors introduced during the process. These errors arise because it is virtually impossible, due to both human and equipment error, to measure process variables exactly or to do precisely what one intends to do while operating the process. The fluctuations

in glass composition can be reduced by taking more process measurements but they can never be completely eliminated.

The hypothetical LFCM process was modeled using a commercially available computer simulation language, SIMAN. Two important features of the model are (1) its ability to simulate simultaneously occurring batch and continuous processes, and (2) its ability to incorporate stochastic variability into the process. The first feature is important because the front end of the hypothetical LFCM process is operated in a batch-wise fashion while the melter itself is operated continuously. The second feature is important because it allows the introduction of uncertainties into the process, which can then be propagated through the system to see how they affect the composition of the glass.

The magnitudes of the uncertainties assumed to characterize the stochastic elements of the process were held constant in all runs of the model. These uncertainties included errors in measuring tank levels, errors in adding glass-forming compounds to the waste, and sampling and analytical errors. There were very few data available on which to base estimates of the magnitudes of the uncertainties, so the modeled uncertainties do not necessarily reflect the errors that will occur in real processes. However, we believe that the modeled uncertainties are reasonable estimates of the true uncertainties. More importantly, we consider the relationship between the errors and the sampling strategies to be representative of the relationship that could be expected in a real process.

Each run of the simulation model simulated 4000 hours of LFCM operation. The output from the runs consisted of "true" and "predicted" glass compositions versus simulated time. The true glass composition was calculated by simultaneously solving all of the mass balance equations describing the system. The predicted glass composition was calculated in the same way, except that stochastic variability was introduced into the calculations, which caused the apparent (i.e., measured) state of the system to deviate from the actual state. Only normal fluctuations in the stochastic variables were modeled; there were no major process upsets introduced into the simulation (i.e., the process was always considered to be "within control limits").

The simulation model was exercised many times to investigate the effects of different sampling and analytical strategies on the ability to control and predict the glass composition. The control objective was to produce a glass with a specified decay heat loading and boron loading. A control algorithm was developed in which upstream sampling of the waste was used in determining the amounts of glass-forming compounds to add to the waste to achieve the target decay heat and boron loading. Control of glass-former addition was necessary because batch-to-batch fluctuations in the incoming waste composition were simulated.

The simulations showed that the glass composition could be better controlled when more samples and more analyses were taken of the waste, and that the composition could be better predicted when more samples and more analyses were taken of the feed. The absolute differences between the true and the target glass compositions were used as a measure of the ability to control the process, and the absolute differences between the predicted and true compositions were used as a measure of the ability to predict glass composition. The 95th percentile points of these differences (95% of the individual absolute differences are less than the 95th percentile point) were calculated for each constituent and each sampling/analytical strategy. The 95th percentile points of the absolute differences between the true and target concentrations of various constituents in the glass were found to be between 2% and 11.5% of the target concentration (depending on the waste sampling and analytical strategy), and the 95th percentile points of the differences between the predicted and true concentrations of various constituents in the glass were found to be between 1.3% and 7.7% of the target concentration (depending on the feed sampling and analytical strategy). The significance of the 95th percentile point of the differences between the predicted and true concentrations (designated here as X% of the target concentration) is that a waste-form producer could place error bands of $\pm X\%$ around the predicted concentration and say, "The true concentration in the glass should fall within these error bands 95% of the time."

It was concluded that the simulation could prove to be an extremely useful tool for investigating the relative costs, risks, and benefits associated with

different sampling and analytical strategies, provided sampling and analytical errors and other process uncertainties can be adequately characterized. Sensitivities of the true and predicted glass compositions to uncertainties in the magnitude of these errors could also be investigated.

The possibility of applying process control charting, a statistical quality control technique, to the operation of the LFCM process was investigated. Control limits were established for the concentrations of various constituents in the feed. Fluctuations of sampled concentrations falling within these control limits are considered to be normal, but when the concentration falls outside these limits, it is an indication that the process has gone out of control. The control limits are narrower when more samples and analyses of either the waste or feed are taken, since this reduces the uncertainty associated with estimates of waste or feed composition.

In order to investigate the ability of the control charts to detect process upsets, streams of random numbers having the same variability and correlation structure as the simulated compositions of the feed were generated using a statistical analysis software package. It was found that a process upset (step change) of 10% from the mean feed composition could not be detected until after 20 batches of feed had been processed (this was true in all cases that were analyzed except for one involving the largest number of samples and analyses of both the waste and the feed, and even in this case the upset could not be detected until after more than 10 batches of feed). This result suggests that if a process upset of 10% or less is considered important, process control charting should be implemented on elements of the process other than just the feed composition. Control charting on other process measurements would 1) lower the inherent process variability and 2) enable the detection of whatever is causing the upset (perhaps a faulty level measurement or a biased analysis of glass former composition) at a much earlier time. Process control charting will be investigated in more detail in future work (see Section 7.0).

A correlation was developed that provides a link between glass composition and the dissolution rate in water. Evaluation of dissolution data for different nuclear waste glasses under near-saturation conditions indicates that the logarithm of rates varies linearly with composite free energy of hydration, in

accordance with theories proposed in the literature. Composite free energy of hydration varies linearly with mole fraction of glass constituents. We found that relative uncertainties in composition of less than 2% will not have a significant impact on the uncertainty in the glass dissolution rate. The results of the process simulation indicate that process variations (excluding upsets) would result in compositional uncertainties on the order of 2% to 11.5% if the assumed standard deviations for stochastic process parameters are correct. Therefore, if it is important to minimize the uncertainty in glass dissolution rate, it would be worthwhile to control the process to the 2% fluctuation level rather than to higher fluctuation levels, which in turn would require more extensive sampling and analyses of the waste. It should be recognized, however, that the glass dissolution rate may be sufficiently low that even with a large amount of uncertainty in the rate it is extremely unlikely that radionuclide release rates will exceed regulatory criteria. If this is the case, it will not be strictly necessary to control the process to the 2% fluctuation level.

The importance of dissolution rate in a repository environment was illustrated by comparing the magnitude of the diffusive flux of radionuclides away from a canister to the magnitude of the flux due to glass dissolution (kinetic flux). The mass transport model used is based on steady-state diffusion away from a spherical waste form in full contact with groundwater. Radionuclides with significant inventories at 1000 years after repository closure were considered, and solubility data from the literature were used to provide a boundary condition on concentration of the waste form. Most radionuclides will be controlled by diffusion because of the low solubility of their elemental species. However, the calculations suggest that up to 11 radionuclides may be controlled by the kinetics of the glass dissolution process. This possibility emphasizes the need for understanding how variations in glass composition, which are inherent in the LFCM process, are related to variations in glass durability.

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1.0 INTRODUCTION

During fiscal year 1982, the U.S. Department of Energy (DOE) assigned responsibility for managing civilian nuclear waste treatment programs in the United States to the Nuclear Waste Treatment Program (NWTP) at the Pacific Northwest Laboratory (PNL). One of the principal objectives of this program is to establish relationships between control of a high-level waste vitrification process and the quality of the glass product. Users of the liquid-fed ceramic melter (LFCM) process will need such relationships in order to establish acceptance of vitrified high-level nuclear waste at a licensed federal repository without resorting to destructive examination of the canisters and their contents.

The work described here will continue through FY-1987 and culminate in a final report on the ability to control and monitor an LFCM process through sampling and process control charting of the feed system. This report describes work done during FY-1986 using a computer simulation model of a representative LFCM process to illustrate relationships between process control and glass product quality and to investigate ways in which performance of the process can be monitored and controlled. The chemical durability of the glass is estimated on the basis of its composition. The durability is of particular interest with respect to acceptance of the glass at a licensed federal repository.

The principal control point for the process is taken to be the monitored composition of the feed as it is mixed in batches from a high-level waste slurry. The mean, variance, and autocorrelation coefficient of the simulated fluctuation of this composition are used to predict the performance of a process control chart in determining shifts in the simulated process, viz. a shift in the mean of the composition of some component. The number of batches that must be monitored before a shift is revealed statistically--termed the "average run length" of the process control chart--is found to depend strongly on the number of samples of feed analyzed and the number of repetitions of analyses per sample. The attending uncertainty in the composition of the product is put into perspective by considering a propagation of this uncertainty, through to the uncertainty in the chemical durability of the product, and finally to the

uncertainty in the performance of the product in a repository setting. The performances of specific waste forms or repositories are not compared or estimated; a "generic" analysis is presented for illustrative purposes only.

1.1 THE WASTE ACCEPTANCE PROCESS

The DOE's Office of Commercial Radioactive Waste Management has instituted a Waste Acceptance Process (WAP) "to outline the documentation and activities required to ensure that waste forms other than spent fuel will be acceptable at any of the potential repositories," and has been instituted because of "the complexity of developing and qualifying waste forms on a schedule that, in some cases, has repository site selection and licensing subsequent to initial waste form production."^(a) To implement this process a Waste Acceptance Committee (WAC) has been established.

The purposes of the WAC are "to concentrate repository project and waste producer contractor resources to focus on the development of waste acceptance requirements, specifications, and other related documentation to advise" the DOE.^(a) It is responsible for coordinating or preparing certain documents called for by the Waste Acceptance Process. The four principal documents are as follows: 1) a Waste Form Description, 2) a Waste Acceptance Preliminary Specification, 3) a Waste Form Compliance Plan, and 4) a Waste Form Qualification Report.

Documents 1, 3, and 4 are developed primarily by the waste producer projects. The Waste Form Compliance Plan must describe how a waste producer proposes to comply with the Waste Acceptance Preliminary Specifications, and the Waste Form Qualification Report must indicate how the producer has shown that the proposed compliance methods have been successfully demonstrated.

(a) "Establishment of Waste Acceptance Process and Waste Acceptance Committee." Memorandum from W. J. Purcell, U.S. Department of Energy, July 8, 1985.

1.2 NWTP APPROACH TO WASTE FORM QUALIFICATION

The Nuclear Waste Treatment Program (NWTP) at PNL is defined as one of the "waste-producing" projects constituting the WAC. The NWTP and its predecessor programs have been developing waste form qualification methods for a number of years; the current programmatic philosophy was described three years ago (Kuhn and Slate 1983). Current work is focused on defining, developing, and demonstrating an objective and quantitative method for assuring the quality of a canister of vitrified high-level waste that is based on process control and statistical monitoring of process instrumentation. The central objective is to address the quality assurance concerns pertaining to disposal of the glass in a licensed nuclear waste repository without sampling the glass from a canister.

The first step in waste form qualification is to define an acceptable vitrified waste product, followed by design of the associated production process. Qualification culminates with acceptance of canisters of vitrified glass for disposal. This approach is patterned after industrial quality control practice as described by Juran, Gyron, and Bingham (1979). The process includes several phases:

Quality of Product Design--establishing the acceptance limits of the intended product

Quality of Process Design--establishing during design and construction of a vitrification plant that the vitrification process will provide a product that falls within the acceptance limits of the intended product

Quality of Conformance--establishing during operation that the actual product falls within the acceptance limits of the intended product.

Accomplishing Quality of Process Design allows Quality of Conformance to be inferred from process operations records. Accomplishing Quality of Product Design allows acceptability of the product to be inferred from Quality of Conformance. Together these allow acceptability of the product to be inferred from operations records. This interrelationship requires that the "intended product" be defined in terms of variables that can be addressed and controlled during operation of the plant.

1.3 OBVIATING DESTRUCTIVE EXAMINATION OF CANISTERS

It is common in the manufacturing industry to determine product quality through contact inspection; often this involves destructive examination. If a batch is found to be defective it could be recycled through the process, relegated to scrap, or shipped under a lesser specification (i.e., a "factory second"), depending on the situation.

These kinds of quality control approaches are not feasible for a process manufacturing canisters of vitrified high-level nuclear waste. Once manufactured, the canisters must be acceptable for disposal in a licensed geologic repository. It would be prohibitively difficult to recycle the glass back into the vitrification process. None of the product can be treated as scrap, and there is no alternative, less-restrictive specification.

Moreover, it would be undesirable to destructively examine a canister in order to obtain a glass sample. Sampling other than through an open canister at the top surface of the glass (which would be difficult) would require coring through the canister wall and into the glass. This process would leave a void in the glass and would require repair of the wall. A part of the waste acceptance specifications pertains to quality assurance of the closure weld. Coring into the canister would hence require that this specification be addressed for a plug weld as well, a very difficult weld compared to the relatively well-controlled welding processes (resistance upset, flywheel/inertial) being considered for the top closure of a canister. Finally, facilities, equipment, and laboratories would have to be provided at additional cost (and perhaps additional worker exposure) to conduct analyses on the glass.

A desirable and feasible alternative to destructive examination of canisters is correlation of glass product quality with information obtained during monitoring and control of the process. For example, one of the most important product attributes is the composition of the glass, which conveys chemical durability, heat load, and radionuclide inventory. Composition is readily amenable to correlation with process sampling and analysis through the use of material balances and statistics.

1.4 ROLE OF PROCESS AND PRODUCT MODELING

The means of inferring the quality of the product from process records are process and product models. The process model translates process records into predicted product characteristics related to composition and structure (e.g., cracking) of the glass, while the product model translates these characteristics into quality characteristics such as the radiation field around a canister or the chemical durability ("leach rate") of the glass.

The role of these models is put into perspective in Figure 1.1. This figure shows a progression of information from the definition of acceptability for the product to a quantification of corresponding quality characteristics. These are translated into product characteristics (using a product model) and, subsequently, to process variables (using a process model). This course defines the intended quality, the intended product provides that quality, and the intended process provides that product. After this information is used to design the process, then actual operation of the process results in a record of process variables describing the actual operation. The recorded data are then translated into the actual product characteristics achieved (using the same process model), thence into the actual quality characteristics achieved (using the same product model), and result finally in a determination of the acceptability of the product.

Two major elements comprise the process model: a thermal model predicting the temperature history of the glass in a canister as it fills and then cools to its final temperature, and a mass balance model predicting the composition of the glass, based on samples taken of the high-level nuclear waste and of the melter feed slurry made from it (see the description of the process, below). Development of the thermal model is proceeding under the NWTP; a code implementing a numerical model of conductive and radiative heat transfer (primarily) is being developed and validated against temperature data obtained from canisters filled with simulated glass and instrumented with thermocouples. The thermal modeling will be reported elsewhere. This report describes work on the mass balance model.

FIGURE 1.1. Role of Process and Product Models

1.5 PURPOSE OF THE PROCESS SIMULATION

The purpose of simulating the LFCM process is to demonstrate how samples of high-level waste and of the corresponding melter feed slurry are combined with other process information to predict the mean and standard deviation of the composition of the glass. No attempt is made to assess the adequacy of the glass expected to be produced by currently identified waste form producers, or to assess the ability to license any of the currently envisioned nuclear waste repositories if vitrified waste were emplaced in them. Instead, the simulation results are an extended approximate and "generic" analysis of product performance. The purpose is to illustrate the kind of information that must be obtained in order to link the predictions of a process model to the acceptability of the product.

The simulation includes stochastic variables to investigate the effect of uncertainties in sample results or imprecise control of process operations on the variability and uncertainty in the glass. Process control charting, a standard industrial technique for monitoring the control of the quality of a product, is introduced as a recommended method to monitor and control an LFCM process.

2.0 DESCRIPTION OF THE SIMULATED LFCM VITRIFICATION SYSTEM

A hypothetical LFCM vitrification system was chosen as the basis for this demonstration of waste form qualification technology. The stream compositions, flow diagram, and process flow rates were adapted from a preliminary flow sheet for a proposed vitrification plant.^(a) A plausible operational strategy was developed; it was based on the tank volumes, flow rates, and in part on strategies commonly discussed for proposed plants. The strategy for controlling the addition of glass formers to the waste was based on the realistic concerns of decay heat loading and boron loading in the glass. Decay heat loading is often mentioned as an acceptance criterion for geologic disposal, and boron content affects the melting rate of the cold cap and the chemical durability of the glass. These two control points were chosen for the sake of example and do not necessarily reflect the concerns of individual waste producers. Indeed, some of the waste producers may be more concerned with compositional variables such as ferrous/ferric ratio or actinide activity than with either decay heat or boron loading.

Melter temperature control was not considered in this demonstration; it was assumed that the temperature of the melter was always in control. The minor temperature fluctuations that occur during the normal operation of a melter are not expected to affect the quality of the glass significantly. The thermal history of the glass after it leaves the melter, however, can be important in that it determines the extent of devitrification and/or cracking in the glass. These glass quality properties may be addressed in acceptance criteria for geologic disposal.

For the purposes of simplifying the simulation, an off-gas system was not considered in this demonstration. All components with melter decontamination factors greater than 1 were assumed to remain entirely in the glass. The exclusion of an off-gas system was probably conservative for waste form

(a) Documented by G. J. Seigny and D. E. Larson in "Preliminary Hanford Waste Vitrification Plant Reference Flowsheet," Hanford Waste Vitrification Program letter report. Pacific Northwest Laboratory, Richland, Washington, 1983.

qualification because most of the volatile components in the melter are expected to adversely affect the quality of the glass. However, a more thorough understanding of melter decontamination factors under various operating conditions and a better understanding of the dependence of glass quality on glass composition are needed before the impact of excluding an off-gas system can be adequately assessed.

2.1 DEFINITION OF WASTE, GLASS FORMERS, AND GLASS

In order to simplify the demonstration, only the seven constituents listed in Table 2.1 are considered to be in the vitrification system. All radioactive decay-heat-producing compounds in the waste are lumped into the constituent called "heat producers," all non-heat-producing compounds in the waste (other than water) are lumped into "other waste," and all glass-forming compounds other than Na_2O , B_2O_3 , and SiO_2 are considered to be "other glass formers." The seven constituents of Table 2.1 are sufficient to demonstrate the control and prediction of decay heat loading and boron loading in the glass. Actually, decay heat loading is not controlled directly, but through the loading of decay-heat-producing compounds. Separate treatment of Na_2O and SiO_2 is not strictly necessary to satisfy the control objectives in this demonstration, but these components are included because Na and Si are expected to have an impact on various measures of product quality (e.g., devitrification, leachability). All constituents are considered to be in their final oxide form at all points

TABLE 2.1. Compositions of Waste, Glass Formers, and Glass^(a) (mass fractions)

	<u>Waste</u>	<u>Glass Former 1</u>	<u>Glass Former 2</u>	<u>Glass</u>
Heat Producers	0.00113	0.0	0.0	0.00844
Other Waste	0.03887	0.0	0.0	0.29
Na_2O	0.0	0.0446	0.0354	0.0703
B_2O_3	0.0	0.012	0.092	0.0912
SiO_2	0.0	0.2988	0.2372	0.47
Other Glass Formers	0.0	0.0446	0.0354	0.0703
Water	0.96	0.6	0.6	0.0

(a) Adapted from Sevigny and Larson report (see footnote on p. 2.1).

in the system. Conversion of chemicals such as nitrates or hydroxides to oxides is not considered because this affects primarily the heat balance in the melter and the throughput of the off-gas system, neither of which is a concern in this demonstration.

The nominal compositions of the waste, glass formers, and glass assumed in this demonstration are listed in Table 2.1. Use of two glass formers permits independent adjustment of decay heat loading and boron loading in the glass. As Table 2.1 indicates, one of the glass formers is boron-rich while the other is boron-lean. A control algorithm (discussed in Section 2.6) is used to determine the amount of each glass former to add to a given batch of waste. The control algorithm is needed to account for random fluctuations in the composition of the waste stream being fed to the vitrification plant (see Section 2.4). If these fluctuations are ignored, they will propagate through the system, possibly resulting in glass that is unacceptable for waste disposal.

2.2 FLOW DIAGRAM

A schematic flow diagram of the LFCM vitrification system is shown in Figure 2.1. There are five major tanks in the system: the Waste Lag Storage Tank (WLST), Waste Concentration Tank (WCT), Feed Preparation Tank (FPT), Melter Feed Tank (MFT), and the melter. The first four tanks are assumed to be well agitated and thus ideally mixed (the melter is also assumed to be ideally mixed, but for other reasons, which will be discussed in Section 3.0). In reality, the tanks will probably not be ideally mixed, but the assumption of ideal mixing was made here in order to simplify the mathematical mass balance equations and thus focus attention on the problem of waste form qualification rather than on the problem of modeling slurry mixing in agitated tanks.

Briefly, the flow of material through the system is as follows: dilute waste slurry is periodically batched to the WLST. From there it is transferred to the WCT, where the slurry is concentrated, by evaporation, to less than one-fourth of the original volume. Once the slurry has been adequately concentrated, it is transferred to the FPT, where glass formers are added and additional evaporation occurs. After the slurry has been adequately concentrated in the FPT, it is transferred to the MFT. Up to this point, all slurry

FIGURE 2.1. Flow Diagram of LFCM Vitrification System

transfers have been in batches. The flow rate of feed from the MFT to the melter, however, is continuous as long as the glass level and cold cap coverage in the melter stay within control limits. If these variables exceed the limits, the feed is shut off until a satisfactory condition is met to continue feeding. Glass is poured from the melter in batches. The flow rates in the system are given in Table 2.2. The stream numbers refer to those given in Figure 2.1. The flow rates for streams F1, F2, F4, F5, F6, and F8 correspond to rapid but brief transfers.

2.3 OPERATIONS

The operational strategy is summarized in this section on a tank-by-tank basis. Each of the items listed in the following subsections represents a decision point or condition for operating the system.

TABLE 2.2. Design Flow Rates in the Vitrification Plant

<u>Stream #</u>	<u>Flow Rate (kg/h)</u>
F1	21,000.0
F2	21,000.0
F3	1,000.0
F4	21,000.0
F5	21,000.0
F6	21,000.0
F7	300.0
F8	21,000.0
F9	152.5
F10	48.8
F11	97.6
F12	103.7

2.3.1 Waste Lag Storage Tank (WLST)

Start transferring waste slurry to WLST: This is done after every other transfer of slurry from the WLST to the WCT (the capacity of the WLST, 70,000 kg, is more than enough to hold two batches of slurry to the WCT).

Stop transferring waste slurry to WLST: This is done when the operators perceive that the level in the WLST has reached 70,000 kg.

2.3.2 Waste Concentration Tank (WCT)

Start transferring slurry from WLST to WCT: This is done when the operators perceive that the level in the WCT has dropped to 2,000 kg.

Stop transferring slurry from WLST to WCT: This is done when the operators perceive that the level in the WCT has risen to 27,000 kg. Also, at the same time that transfer from the WLST to the WCT is stopped, evaporation of water from the WCT is initiated.

Stop evaporation of water from WCT: This is done when the operators perceive that the level in the WCT has dropped to 7,808 kg.

2.3.3 Feed Preparation Tank (FPT)

Start transferring slurry from WCT to FPT: This is done when the operators perceive that the level in the FPT has dropped to 2,000 kg. However, before transfer is initiated, the operators must first check to see whether the slurry in the WCT has been adequately concentrated. If it has not, the FPT will remain at a level of 2,000 kg until the slurry in the WCT is ready for transfer. When transfer is initiated, addition of the two glass former slurries is also initiated.

Stop transferring slurry from WCT to FPT: This is done when the operators perceive that the level in the WCT has dropped to 2,000 kg. This step coincides with "Start transferring slurry from WLST to WCT" (above).

Stop adding glass formers to FPT: This is done according to the control algorithm for addition of glass former, discussed in Section 2.6.

Start evaporating water from FPT: This is done after transfer of slurry from the WCT to the FPT or after addition of glass formers to the FPT, whichever takes longer. If the operators perceive that the level in the FPT is below 12,467 kg after the transfer of waste slurry and the addition of glass formers, then the evaporation of water is not initiated.

Stop evaporating water from FPT: This is done when the operators perceive that the level in the FPT has dropped to 12,467 kg. However, if the operators perceive that the level is less than 12,467 kg after transfer of waste from the WCT and addition of glass formers, evaporation of water is never initiated (see "Start evaporating water from FPT").

2.3.4 Melter Feed Tank (MFT)

Start transferring slurry from FPT to MFT: This is done when the operators perceive that the level in the MFT has dropped below 5,000 kg. However, before transfer is initiated, the operators must first check to see whether the slurry in the FPT has been adequately concentrated. If it has not, the transfer is delayed until the level in the FPT reaches a point that indicates sufficient concentration (12,467 kg). Meanwhile, slurry will continue to be transferred from the MFT to the melter, thus reducing the level in the MFT below 5,000 kg.

Stop transferring slurry from FPT to MFT: This is done when the operators perceive that the level in the FPT has dropped below 2,000 kg. This step coincides with "Start transferring slurry from WCT to FPT" (see above).

2.3.5 Melter

Stop transferring slurry from MFT to Melter: This is done under any of the following three conditions:

- 1) The operators perceive that the level in the MFT has dropped below 2,000 kg.
- 2) The operators perceive that the mass of the cold cap exceeds 500 kg. This is equivalent to saying that the cold cap coverage exceeds some critical value.
- 3) The operators perceive that the total mass of glass plus cold cap in the melter exceeds 5,000 kg.

Start transferring slurry from MFT to Melter: This is done to restart the feed after a stoppage has occurred due to any of the above three conditions. The restart occurs under any of the following conditions (all conditions must be met before feeding is initiated):

- 1) The operators perceive that the level in the MFT has risen above 2,050 kg.
- 2) The operators perceive that the mass of the cold cap has dropped below 450 kg.
- 3) The operators perceive that the total mass of glass plus cold cap in the melter has dropped below 4,800 kg.

Stop pouring glass into canister: This occurs under one of the following conditions:

- 1) The operators perceive that the amount of glass in the canister currently being filled has exceeded 1,500 kg, indicating that the canister is full.
- 2) The operators perceive that the total mass of glass plus cold cap in the melter has dropped below 2,800 kg.

Start pouring glass into canister: This occurs under one of the following conditions:

- 1) 15.37 hours has elapsed since the last canister was filled. This provides adequate time for the level of glass plus cold cap in the melter to reach the level that existed prior to filling the last canister.
- 2) The operators perceive that the total mass of glass plus cold cap in the melter has risen above 3551 kg (having previously been lower).

2.4 UNCERTAINTIES IN PROCESS PARAMETERS

Several process parameters have values that are inherently uncertain because they cannot be measured or controlled exactly. These uncertainties (hereafter called "process uncertainties") give rise to fluctuations in the values of the process variables over time. It is assumed that the process uncertainties are random and are normally distributed about some mean. The fluctuations in the process variables, therefore, will also be random and will be normally distributed about some set of target or design values.

The process uncertainties used in this analysis are shown in Table 2.3. These are given in the form of a mean and a standard deviation that define a normal distribution. There is assumed to be a 5% relative standard deviation (RSD) in the concentration of waste constituents from one waste batch to the next, a 1% RSD of full-scale reading for tank level measurement, a 2% RSD in the concentration of glass former constituents in successive batches to the FPT, a 2% RSD in the amount of glass formers added to the FPT (2% relative to the amount that should have been added according to the control algorithm for glass former addition), and a 2% RSD in the time elapsed between filling a canister and starting to fill the next canister. All but the last uncertainty will be propagated through the system, giving rise to time-varying fluctuations in the composition of the glass.

The uncertainties listed in Table 2.3 are intended to be realistic for the operation of an LFCM vitrification system. The magnitude of the relative standard deviations that describe the uncertainties, however, are merely educated

TABLE 2.3. Uncertainties in Process Parameters

Parameter	Mean	Standard Deviation
Mass Fraction of "Heat Producers" in Batches of Waste	0.00113	0.0000565
Mass Fraction of "Other Waste" in Batches of Waste	0.03887	0.001945
Full Level in WCT, kg	27000.0	270.0
Level in WCT Corresponding to Adequate Concentration, kg	7808.0	270.0
Empty Level in WCT, kg	2000.0	270.0
Level in FPT Corresponding to Adequate Concentration, kg	12467.0	130.0
Empty Level in FPT, kg	2000.0	130.0
Level in MFT at which Transfer from FPT can begin, kg	5000.0	150.0
Empty Level in MFT, kg	2000.0	150.0
Mass Fraction of Na_2O in Glass Former 1	0.0446	0.000892
Mass Fraction of B_2O_3 in Glass Former 1	0.012	0.00024
Mass Fraction of SiO_2 in Glass Former 1	0.2988	0.005976
Mass Fraction of "Other Glass Formers" in Glass Former 1	0.0446	0.000892
Mass Fraction of Na_2O in Glass Former 2	0.0354	0.000708
Mass Fraction of B_2O_3 in Glass Former 2	0.092	0.00184
Mass Fraction of SiO_2 in Glass Former 2	0.2372	0.004744
Mass Fraction of "Other Glass Formers" in Glass Former 2	0.0354	0.000708
Added Amount of Glass Former 1	(a)	2.0% of Mean
Added Amount of Glass Former 2	(a)	2.0% of Mean
Time Between Canister Pours, h	15.37	0.3074

(a) To be determined by the glass former addition algorithm.

guesses for which there are little supporting data. The 5% RSD in the concentration of waste constituents from batch to batch could result from the nonuniform distribution of solids (due to imperfect mixing) in tanks that are upstream of the WLST. Since tank levels are given as masses, the 1% error in reading levels could be due to error in measuring the height of the slurry in a tank (which provides an estimate of volume) or to error in measuring the density in a tank, which is needed for the conversion of volume to mass. The 2% RSD in the concentration of glass-forming constituents added to the FPT could be caused by errors in preparing the glass-forming slurry or to errors in sampling and analyzing the slurry. The 2% RSD in the amount of glass formers added to the FPT relative to that which the control algorithm prescribes could result from operator error or nonuniform flow of the concentrated slurry into the FPT. Operator error would be the most likely cause of the 2% RSD in the time between canister fills.

2.5 WASTE SAMPLING AND ANALYSIS

Each time the WLST is charged with incoming waste, its contents are sampled. The samples are taken one hour after the transfer of waste to the WLST is completed in order to allow time for mixing between the new waste and the WLST heel. The accuracy and precision of composition estimates of the slurry in the WLST will depend on how many samples are taken and how many analytical determinations are made on these samples. Various sampling and analysis strategies are possible, ranging from a single analysis of a single sample to replicate analyses of replicate samples. The estimate of composition in the latter case would be the average of all the analytical determinations. Obviously, more samples and more analyses will provide a better estimate of the true composition, but at a higher cost and over longer time. The average of all the analytical determinations of samples from a given batch of WLST waste is used in the control algorithm to determine the amounts of the two glass formers to add in the FPT (see Section 2.6).

It follows from the previous paragraph that each analytical determination of composition in the WLST has two sources of error associated with it: sampling error and analytical error. "Sampling error" is defined as the

difference between the true composition in the tank and the composition of a sample taken from the tank. Sampling errors may be due to variability in sampling technique, or they may represent a true variation of composition in the tank as a function of position and/or time. "Analytical error" is defined as the difference between the true composition of a sample and the apparent composition as determined by some analytical procedure. Analytical errors may be due to errors in preparing the sample for analysis, errors in the calibration of analytical instruments used in the analysis, and/or errors resulting from the finite tolerances of the analytical instruments. Sampling and analytical errors may be different for each constituent that is analyzed.

In this demonstration it is assumed that the sampling error associated with each waste constituent in the WLST is described by a normal distribution having a mean equal to the true concentration of that constituent in the WLST (assuming an ideally mixed tank) and a standard deviation of 5% of this mean (5% RSD). A 5% RSD is also assumed for the analytical error associated with waste constituents in WLST samples (the mean in this case is the true concentration in the sample). These are conservative estimates, based on data obtained at the West Valley Demonstration Project.^(a)

2.6 CONTROL ALGORITHM FOR GLASS FORMER ADDITION

Since the apparent composition of the slurry in the WLST is known from sampling and analysis, and since the amounts of slurry transferred from the WLST to the WCT and from the WCT to the FPT are known, an estimate can be made of the quantities of waste constituents in each batch fed to the FPT. The calculations performed to make these estimates are complicated in that the WCT heel after transferring to the FPT must be taken into account in subsequent batches. If the quantities of waste constituents batched to the FPT are known, the necessary additional amount of the two glass formers can be determined by a calculation involving two equations in two unknowns.

(a) Documented by W. M. Bowen and B. A. Pulsipher in "Sampling Plan for the WVDP Feed Concentrator Make-Up Tank," NWTP Letter Report to West Valley Demonstration Project. Pacific Northwest Laboratory, Richland, Washington, 1985.

In order to determine the amount of glass formers to add to the FPT, an estimate must be made of the composition of the waste slurry that is batched to the FPT. This composition will be the same as the composition of the contents of the WCT. As described in Section 2.3.2, every time the WCT is emptied, 5,808 kg of slurry is transferred to the FPT, and 2,000 kg (or 25.6%) is left behind. Assuming ideal mixing, 25.6% of the heel (or 6.6% of the total) remains from the heel of the previous batch. This calculation could be carried out repeatedly to get the contribution of every previous batch to the composition of the current batch. The 5,808 kg of slurry transferred from the WCT to the FPT represents concentrated material from 25,000 kg of slurry originally transferred from the WLST to the WCT. If one is sampling the WLST, therefore, the mass of a given constituent that is entering the FPT because of each of N previous batches from the WLST to the WCT is given by the following equations:

$$M_{xi} = C_{xi} * 25000.0 * (5808/7808) \quad (2.6.1)$$

$$M_{x(i-j)} = C_{x(i-j)} * 25000.0 * (5808/7808) * (2000/7808)^j \quad (2.6.2)$$

$$M_{x(i-N)} = C_{x(i-N)} * 25000.0 * (2000/7808)^N \quad (2.6.3)$$

where: M_{xi} = the portion (in mass units) of the total mass of constituent x being transferred to the FPT that was contributed by WCT batch i (the most recent WCT batch)

C_{xi} = concentration of constituent x in WCT batch i as determined from sampling the WLST

$M_{x(i-j)}$ = the portion (in mass units) of the total mass of constituent x being transferred to the FPT that was contributed by the jth previous WCT batch

$C_{x(i-j)}$ = concentration of constituent x in the jth previous WCT batch as determined from sampling the WLST

j = 1 to (N-1)

N = total number of previous batches to be taken into account.

The total mass of constituent x in the current batch to the FPT is given by

$$M_x = \sum_{j=0}^n M_{x(i-j)} \quad (2.6.4)$$

In this demonstration, the two quantities being controlled are the decay heat loading and the boron loading in the glass. To determine the amount of each glass former to add to the FPT batches, therefore, the total mass of waste solids, M_w , and the fraction of these solids that are heat producing compounds, X_{hw} , must be known for each FPT batch. These quantities could be calculated from Equations 2.6.1 through 2.6.4 ($X_{hw} = M_h/M_w$).

Once X_{hw} and M_w are known, the amounts of each glass former to add to the FPT can be calculated by simultaneous solution of the mass balance equations for decay-heat-producing compounds and boron around the FPT (dry basis):

$$\text{Heat:} \quad X_{hw} * M_w = X_{hg} * (M_w + M_1 + M_2) \quad (2.6.5)$$

$$\text{Boron:} \quad X_{b1} * M_1 + X_{b2} * M_2 = X_{bg} * (M_w + M_1 + M_2) \quad (2.6.6)$$

where: M_1 = Mass of glass former lean in B_2O_3 added to the FPT (dry basis)
 M_2 = Mass of glass former rich in B_2O_3 added to the FPT (dry basis)
 X_{b1} = Mass fraction (on a dry basis) of B_2O_3 in glass former 1
 X_{b2} = Mass fraction (on a dry basis) of B_2O_3 in glass former 2
 X_{hg} = Target mass fraction of decay-heat-producing compounds in glass
 X_{bg} = Target mass fraction of B_2O_3 in glass.

Table 2.1 gives the following values:

$$\begin{aligned} X_{b1} &= 0.03 \\ X_{b2} &= 0.23 \\ X_{hg} &= 0.008435 \\ X_{bg} &= 0.0912. \end{aligned}$$

Simultaneous solution of Equations 2.6.5 and 2.6.6 for M_1 and M_2 gives

$$M_1 = M_w * \frac{x_{b2} * (\frac{x_{hw}}{x_{hg}} - 1) - x_{bg} * \frac{x_{hw}}{x_{hg}}}{x_{b2} - x_{b1}} \quad (2.6.7)$$

$$M_2 = M_w * \frac{x_{bg} * \frac{x_{hw}}{x_{hg}} - x_{b1} * (\frac{x_{hw}}{x_{hg}} - 1)}{x_{b2} - x_{b1}} \quad (2.6.8)$$

To get the actual amount of glass former 1 and glass former 2 to add to the FPT, M_1 and M_2 must be divided by the mass fraction of solids in the glass formers (0.4 in this case). So $M_1/0.4$ and $M_2/0.4$ are the amounts of glass former 1 and glass former 2, respectively, to add to the FPT to get as close as possible to the target composition in the glass. The resulting glass will not have the target composition; rather, it will be a product that varies randomly about the target composition. This deviation is a consequence of the sampling and analytical errors associated with measuring the composition of the slurry in the WLST, errors in reading levels in tanks, errors in glass former make-up, and errors in transferring quantities of glass formers to the FPT.

2.7 FEED SAMPLING AND ANALYSIS

It is assumed that a sample (or samples) of the combined waste and glass former feed slurry will be taken in the FPT before transfer to the MFT. This step will provide a measure of how close the feed is to the target composition. The apparent composition can then be used to predict the final glass composition by using the mass balance model discussed in Section 3.0.

As with the WLST, the difference between the true composition and the apparent composition of the FPT will depend on the magnitude of the sampling and analytical errors associated with the constituents in the FPT and on the sampling and analytical strategies employed. The sampling and analytical errors for the waste constituents in the FPT are assumed to be described by normal distributions with a 5% RSD. The glass-forming constituents are assumed to have sampling and analytical errors described by normal distributions with a 4% RSD. These RSD values are based on data reported in Bowen and Pulsipher's 1985 letter report (Section 2.5). Assigning different RSD values for waste

constituents and the glass-forming constituents implies that there are no constituents common to both the waste and the glass formers. This is probably unlikely, but it is assumed here to simplify the demonstration.

An option that could be exercised during operation of the vitrification plant is to hold the feed slurry in the FPT until analyses of the feed samples are completed. This procedure would enable the operators to react to batches that deviate significantly from the target composition (in an unacceptable direction) by adding more glass formers to the FPT slurry. However, these adjustments would be made knowing only the apparent FPT composition, which varies randomly from the true composition through the sampling and analytical errors. It is possible, therefore, that one could make adjustments when they are not warranted. A statistical basis for deciding when to take control action is discussed in the next section.

2.8 PROCESS CONTROL CHARTING

A standard technique for monitoring the quality of the waste glass is the implementation of statistical process control (SPC) methods. The SPC methods have been widely accepted as a simple but powerful tool for controlling quality in a manufacturing environment. Their purpose is twofold: controlling the level of quality of a process by flagging anomalies where the process is not stable or has shifted, and improving the quality through an increased understanding of the variables that influence the process. The LFCM vitrification technology can benefit from SPC because it is a new process and because there is a desire to produce quality glass without final sampling of the product. A more detailed treatment of SPC as applied to the LFCM system has been documented by Pulsipher.^(a)

The basis for SPC is that the quality of a manufactured product is always subject to some variation naturally inherent in the process because of stochastic mechanisms. When the process is stable (under control), the behavior of the variation of the measurements is according to some random pattern. SPC

(a) B. A. Pulsipher. "Statistical Process Control Applied to the Liquid Fed Ceramic Melter." Being prepared by the Nuclear Waste Treatment Program, Pacific Northwest Laboratory, Richland, Washington.

focuses on detecting fluctuations that are greater than those expected from random variations. A principal tool for detecting those fluctuations is the Shewhart control chart.

2.8.1 Theory of Control Charts

The statistical theory of control charts is founded in the central limit theorem. This theorem states that the form of the probability distribution of sample means approaches the form of a normal probability distribution as the size of the sample is increased, regardless of the distributions describing the individual samples used to calculate the sample means. For a normal distribution, 68% of values selected randomly will fall within ± 1 standard deviation of the mean, 95% fall within ± 2 standard deviations, and 99.7% within ± 3 standard deviations. The Shewhart control chart establishes control limits at ± 3 standard deviations from the mean of a process variable being monitored. The process mean and standard deviation must be determined when the process is stable (under control), during which time 99.7% of the measurements should fall within the process control limits. When measured values fall outside these limits, it is taken as evidence that the process fluctuations are not part of the random fluctuation inherent in the process, and the process is determined to be out of control.

2.8.2 Implementing Control Charts for an LFCM Process

Process control charting could be implemented at various stages of the LFCM process and within the analytical laboratory. For the purpose of this report, control charts are applied to samples taken from the FPT after glass former addition and evaporation. In this case, the average composition in the FPT is considered to be the "process average." The composition of the material from the current FPT batch can be determined by subtracting the contribution of the heel from the previous batch. Adjusted FPT compositions are used here on SPC. A basic assumption is that SPC is applied to the analytical laboratory and that the laboratory is in statistical control. Given this, any process measurements observed to be outside the control limits would be due to changes in the process mean or standard deviation, and not due to changes or bias in the analytical laboratory.

The standard deviation of the process average can often be separated into different components. If control charts are applied to samples taken from the FPT, there is variability inherent in the process (upstream of the sampling point), variability among replicate samples taken from the same FPT batch (sampling error), and variability among replicate analyses of the same sample (analytical error). The process variability will be influenced by all of the process uncertainties described in Section 2.4 except the uncertainty in the time between batch canister pours. Since errors associated with sampling and analyzing samples from the WLST are propagated through the glass former addition control algorithm and will ultimately affect the amount of glass formers added to the FPT, these errors also influence the process variability. Because the combined effect of all these sources of variability is difficult to quantify, the overall process variability is best estimated by running the process or simulating a run of the process when it is in control. Control limits that allow for inherent process variability can then be established.

The specific application of control charting in this demonstration is tied to the specifics of the simulated process. Each time the WLST is filled, the composition of the incoming waste mix is randomly selected from a normal distribution of possible waste mix compositions. The apparent waste and heat concentration in the WLST is used in the glass former addition algorithm to determine the amount of glass formers to add to two successive batches of feed made up in the FPT (one batch in the WLST is the volume equivalent of two batches in the FPT). Thus there is some correlation between two FPT batches made from the same WLST batch.

The waste glass process has other characteristics that set it apart from normal applications where control charts are used. As noted in Section 2.6, when a tank is ready to be filled, it contains a heel remaining from the previous tankful. This heel causes a correlation between the previous tank composition and the current tank composition. In the usual application of control charts, the assumption of independence of charted observations is required.

The simulated FPT compositions were studied to determine the effects of the above-mentioned correlations. A statistical technique for examining the correlation structure of data produced over time is autoregression.

Autoregression allows the next deviation from the target composition in the FPT to depend partly upon previous deviations. For example, if the heat producers were higher than the target value for previous FPT batches, the next FPT batch may show a high value for heat producers if the correlation is large. Applying this technique to the simulated data revealed that a first-order autoregressive model adequately described the correlation structure for the boron, silicon, and sodium oxides. However, there appeared to be no significant correlation over time for heat producers and other waste. This suggests that the usual control chart methods may be applied to the heat and waste compositions. In the case of these constituents, the process variance, S_p^2 , of the apparent composition of individual FPT batches is calculated as follows:

$$S_p^2 = \sum_{i=1}^n \frac{(Y_i - \bar{y})^2}{n-1} \quad (2.8.1)$$

where the Y_i are the apparent compositions of individual FPT batches, and $\bar{y}$ is the overall average of the apparent compositions of individual batches.

The method for calculating the process variance for the boron, silicon, and sodium constituents will now be discussed. The variance of an observation with the correlation structure of a first-order autoregressive model is

$$\sigma_p^2 = \frac{\sigma_v^2}{1-\rho^2} \quad (2.8.2)$$

where σ_v^2 is random variance and ρ is the correlation between the current observation and the previous observation. The estimates of σ_v^2 and ρ are easily obtained from simulated data for each constituent ($\rho=0$ for heat producers and other waste). If the variance of the n data points for each constituent were calculated as in Equation 2.8.1, then it can be shown that the value S_p^2 on the average tends to estimate

$$S_p^2 = \sigma_p^2 \left(1 - \frac{2\rho}{n}\right) \quad (2.8.3)$$

In the case of the simulation, n is sufficiently large to say

$$S_p^2 = \sigma_p^2 = \frac{\sigma_v^2}{1-\rho^2} \quad (2.8.4)$$

Because S_p^2 incorporates information about the correlation structure and is an estimate of the process variance of the apparent composition of individual FPT batches, it can be used to set up the control limits for individual FPT batches.

Up to this point, the variance discussed excludes the sampling and analytical variabilities, S_s^2 and S_a^2 , respectively. These variances are incorporated into the total variability as follows:

$$S_{Tot}^2 = S_p^2 + \frac{S_s^2}{n_s} + \frac{S_a^2}{n_a * n_s} \quad (2.8.5)$$

where n_s is the number of samples taken from each FPT batch, and n_a is the number of analytical determinations per sample. Control limits for each constituent (including heat and waste compositions) could be calculated by

$$\bar{Y}_i \pm 3 \sqrt{S_{Tot,i}^2} \quad (2.8.6)$$

where $\bar{Y}_i$ is the average composition for the i th constituent (in the simulation, $\bar{Y}_i$ is the target composition). When the apparent FPT composition for any constituent falls outside either control limit developed for that constituent, the process is considered to be out of control.

The control chart described above is for individual FPT batches instead of the average of several batches. The central limit theorem, which states that the probability distribution of sample means approaches the form of a normal distribution regardless of the distribution of individual samples, does not apply here because the individual FPT batch is only one sample (not an average of several batches) from the population of FPT batches. When this theorem cannot be applied, individual FPT batches must form a normal distribution in order

to apply the normal probability control chart techniques. The simulated data were checked to determine whether individual FPT batches were normally distributed. This assumption of normality appeared to hold true.

The control chart detects shifts in the process average. Some changes in the process could affect the variance of the process without causing a shift in the process average. One additional control chart to monitor the variability of the process would be useful. A simple measure of the variability is the range of the composition of adjacent FPT batches. For each FPT batch, this moving range would be calculated by the difference between the current FPT composition and the FPT composition in the previous batch. An average range, $\bar{R}$, would be calculated to set up the control limits. This control chart is often referred to as a moving range chart. The lower control limit is zero, and the upper control limit is

$$\text{Upper Limit} = 3.27 * \bar{R} \quad (2.8.7)$$

The 3.27 is obtained from a table containing control chart factors for range charts.

The above approaches for setting up a control chart require at least 10 observations. Because many of the vitrification projects may be limited in the number of FPT batches and because most investigators are interested in obtaining information concerning the quality of the product near the beginning of processing, it would be wise to use simulated data to obtain an estimate for inherent process variation to initially set up control charts. Estimates of the magnitudes of individual process uncertainties that factor into the overall process variability can probably be made during prototyping or cold testing prior to actual processing of radioactive waste.

3.0 MASS BALANCE MODEL

An essential part of this demonstration of waste form qualification technology was the development of a mass balance model of the vitrification plant. To investigate the effects of process uncertainties, sampling and analytical error, and process upsets, something more than a direct steady-state solution of the governing mass balance equations is required. The approach taken was to develop a dynamic simulation model of the vitrification plant. This was done using the commercially available computer simulation language, SIMAN, which is written entirely in FORTRAN and requires only a FORTRAN compiler to be run on a computer system. The following sections contain first a summary of all the assumptions that are built into the mass balance model, and then a description of how the model was implemented using the SIMAN simulation language.

3.1 ASSUMPTIONS

In simulating the LFCM vitrification system described in Chapter 2.0, the following assumptions were made:

1. There is no volatilization or entrainment of constituents other than water in any of the evaporation streams or in the melter off-gas stream.
2. There is a lag of 24 hours between the time when samples are taken and the time when analyses of the samples are available.
3. The melter contains two regions that are modeled separately: the cold cap and the molten glass.
4. Both the cold cap and the molten glass are assumed to be ideally mixed regions. This assumption appears to be valid for PNL's pilot-scale ceramic melter.^(a) For the purposes of this demonstration, the

(a) Documented by W. L. Kuhn et al., in "Report on Progress on Waste Form Qualification Mass Balance Modeling." NWTP Internal Letter Report. Pacific Northwest Laboratory, Richland, Washington. 1985.

settling or floating of minor phases is ignored, although it is recognized that this could ultimately be a concern.

5. The melting rate of the glass (i.e., the rate of mass transfer from the cold cap to the molten glass) is determined by the B_2O_3 content of the cold cap. This dependence is described by

$$\text{Melting rate (kg/h)} = 1.7836 * X_{bc} * M_c \quad (3.1)$$

where X_{bc} = weight fraction of B_2O_3 in the cold cap
 M_c = total mass of the cold cap.

6. All of the feed to the melter is assumed to go into the cold cap (except the water, which goes to the off-gas system). In other words, none of the feed bypasses the cold cap and goes directly into the molten glass.
7. Cold cap coverage is maintained to an extent equivalent to 300 kg of cold cap mass.
8. The temperature of the melter is always within its control limits.

As discussed in Section 2.6, the control algorithm for addition of glass formers requires a calculation to correct for the heel in the WCT. This correction takes into account the contributions of the previous N batches to the heel (see Equations 2.6.1, 2.6.2, and 2.6.3). In this model, N was taken to be 2. This assumption introduces a slight error because it neglects all but the two most recent batches; in reality these two batches contribute only about 94% of the heel, with the remaining 6% coming from earlier batches.

3.2 USE OF THE SIMAN SIMULATION LANGUAGE

The SIMAN simulation language is set of FORTRAN subroutines that can be used in conjunction with user-written FORTRAN subroutines to model systems undergoing continuous changes in state, discrete changes in state, or any combination thereof (Pegden 1985). The latter capability has been applied here because the vitrification plant is represented by both continuous and batch processes. Another key feature of the SIMAN code is the ability to incorporate

stochastic variability into models. This is done through an extensive library of statistical distribution functions and through the use of an internal random number generator, which is used to randomly select values from specified statistical distributions.

The following sections summarize how SIMAN was used to model the vitrification plant. A detailed description of the SIMAN language is provided in the text by Pegden (1985).

3.2.1 Continuous Aspects of the Mass Balance Model

Since the mass balance model is a dynamic simulation model, the mass of each constituent in each of the tanks changes continuously with time. These changes are described by differential equations of the form

$$d(\text{total mass})_j/dt = \sum_{k=1}^K \{\text{mass flow rate in}\}_k - \sum_{l=1}^L \{\text{mass flow rate out}\}_l \quad (3.2.1)$$

$$d(\text{mass})_{ij}/dt = \sum_{k=1}^K \{\text{mass flow rate in}\}_{ik} * \{\text{mass fraction}\}_{ik} - \sum_{l=1}^L \{\text{mass flow rate out}\}_{il} * \{\text{mass fraction}\}_{il} \quad (3.2.2)$$

where i = species index

j = tank index

k = index of streams going into tank j

l = index of streams going out of tank j

K = number of streams going into tank j

L = number of streams going out of tank j .

These equations represent a mass balance around an ideally mixed tank. Since ideal mixing is assumed, the composition of any stream in the system is the same as the composition in the tank from which it originated:

$$\{\text{mass fraction}\}_{ij} = \{\text{mass fraction}\}_{ij} \quad (3.2.3)$$

The mass fraction in any given tank is given by the following equation:

$$\{\text{mass fraction}\}_{ij} = \{\text{mass}\}_{ij} / \{\text{total mass}\}_j \quad (3.2.4)$$

A complete set of the mathematical equations used in the vitrification system mass balance model is given in Appendix A. Most of these equations are species- and tank-specific forms of Equations 3.2.1, 3.2.2, and 3.2.4. A description of the variables appearing in Appendix A is given in Appendix B.

The differential and state equations of Appendix A are simultaneously solved using a Runge-Kutta-Fehlberg numerical differentiation algorithm that is part of the SIMAN subroutine library. The Runge-Kutta-Fehlberg algorithm is a variable-step-size, fourth-fifth-order approximation technique. SIMAN allows the user to choose the minimum and maximum step sizes that the algorithm is to take for each time step and the maximum relative and absolute truncation errors that can be tolerated at each step. The algorithm will then adjust the step size between the minimum and maximum until the truncation error conditions are met.

3.2.2 Discrete Events

During the operation of the vitrification plant, many events occur at discrete points in time. In simulation jargon, these events are called "discrete events." Examples of discrete events include turning on/shutting off a pump (or valve), starting/stopping the transfer of material from one tank to another, sampling a tank, or starting/stopping the pouring of glass into a canister. Discrete events are triggered either by a condition on time or by a condition on one or more state variables that describe the state of the system. An example of the former is the sampling of a tank every 24 hours. An example of the latter is turning on a pump to transfer slurry into a tank whose level has dropped below a certain limit. Discrete events can interact with state variables to alter the state of the system and/or the rate of change of the state of the system.

Table 3.1 gives a summary of all the discrete events that are built into the mass balance model and the condition(s) under which these events are triggered. Many of the events correspond to the operational decision points and conditions discussed in Section 2.3. Internal SIMAN subroutines keep track of simulated time and the values of all the state variables, so SIMAN knows exactly when to execute any discrete event that is conditional on time or on the state of the system.

3.2.3 Stochastic Variability in the Mass Balance Model

The mass balance model contains a number of parameters that vary stochastically with time. These parameters include all the uncertainties listed in Table 2.4 as well as the sampling and analytical errors associated with measuring concentrations in tanks. All the uncertainties are assumed to be described by normal distributions. To account for stochastic variability in the system, the mass balance model takes advantage of SIMAN subroutines that provide random sampling of user-defined distributions.

3.2.4 Simulation of the Vitrification Plant

In this demonstration, the system was always initialized to the target or design values of all variables. Thus, the system always started out in an "ideal" state and fluctuated about that ideal point as uncertainties crept in and were propagated. The initial values of all state variables in the system are given in Appendix C. These values also represent the time-persistent means of the variables over long periods of simulation time.

The simulation program maintains an internal clock that keeps track of simulated process time. Control is initially passed to the subroutine containing the Runge-Kutta-Fehlberg numerical differentiation algorithm, which steps through time solving the differential and state equations of Appendix A. Step size is automatically determined by truncation error criteria. As time is advanced, SIMAN subroutines constantly check to see if any of the state variables cross values that trigger discrete events. When one of these values is crossed, control is passed to a subroutine that contains statements describing changes to the state of the system that are associated with the event. Time is not advanced during a call to one of the event subroutines. If the

TABLE 3.1. Discrete Events in the Mass Balance Model

Event	Condition(s)
Turn off flow of waste into WLST	Level in WLST exceeds 70,000 kg
Turn on flow of waste from WLST into WCT, start evaporation from FPT	Level in WCT drops below 2,000 kg
Turn off flow of waste from WLST into WCT, start evaporation from WCT	(1) Level in WCT exceeds 27,000 kg (2) Level in WLST drops to 2,000 kg
Stop evaporation from WCT	Level in WCT drops to 7,808 kg
Turn on flow of slurry from WCT into FPT, add glass formers to FPT	(1) Level in FPT drops below 2,000 kg (2) Level in WCT is at 7,808 kg
Stop evaporation from FPT, start sampling the FPT	Level in FPT drops to 12,467 kg
Turn on flow of slurry from FPT into MFT	(1) Level in MFT drops below 5,000 kg (2) FPT sampling is complete
Turn off flow of slurry from MFT into Melter	(1) Level in MFT drops below 2,000 kg (2) Mass of cold cap exceeds 500 kg (3) Mass in Melter exceeds 4,800 kg
Turn on flow of slurry from MFT into Melter	(1) Level in MFT rises above 2,050 kg (2) Mass of cold cap drops to 450 kg (3) Mass in Melter drops to 4,500 kg
Stop pouring glass into Canister	(1) Mass in Canister exceeds 1,500 kg (2) Mass in Melter drops to 2,800 kg
Start pouring glass into Canister	(1) It is 15.37 hours since last pour (2) Mass in Melter rises above 3,551 kg
Take sample from WLST	It is 1 hour after filling the WLST
Sampling of FPT is complete	It is 0.2 hour after sampling started
Analyses of WLST samples are complete	It is 24 hours after sampling WLST
Turn on flow of waste into WLST	Level in WCT exceeds 27,000 kg and the WLST was not filled the last time this happened
Calculate the amounts of glass formers 1 and 2 to add to the FPT	It is 0.1 hour after analyses of WLST samples were completed
Turn off flow of glass former 1 into FPT	The amount of glass former 1 prescribed by the glass former control algorithm has been added
Turn off flow of glass former 2 into FPT	The amount of glass former 2 prescribed by the glass former control algorithm has been added

event occurs over a finite time duration, an event that corresponds the end of the current event must be scheduled at some time in the future. This is done by scheduling the event corresponding to the end-of-event onto the event calendar, a special file maintained by SIMAN that contains an ordered list of all the events that are to occur in the future and the time at which they are to occur. When the simulation clock advances to one of the times on the event calendar, a call is made to the appropriate event subroutine. Event subroutines are generally written by the user, as the events are specific to the system being simulated. An event does not necessarily have to affect the state of the system or correspond to the end of an event; it may be used simply to write values to an output file or to manipulate values to get specific pieces of information out of the simulation. The simulation ends when the internal clock reaches a predetermined stopping time.

3.2.5 Predicted Values versus True Values

The mass balance simulation model constantly tracks the "true" values of all the state variables in the system. It does this by simultaneous solution of the state and differential equations in Appendix A. The predicted values of the state variables at any point in the system are based on the apparent compositions in the WLST and FPT when these tanks are sampled. As described in Section 2.6, the apparent composition in the WLST (i.e., the composition inferred from sampling and analysis) is used to calculate the amount of each of the two glass formers to add to the FPT. The apparent composition in the FPT can be used either to calculate how much additional glass former slurry should be added to the FPT to adjust the composition closer to the target, or to predict what the final glass composition will be if no corrective action is taken. In this demonstration, it was assumed that no adjustment was made, so the information from FPT samples was used exclusively to predict final glass composition.

The predicted glass composition was calculated from the apparent composition in the FPT. The calculation involved plugging the apparent FPT composition into the exact same set of mass balance equations used to calculate the "true" composition in the MFT, cold cap, and molten glass (see Appendix A). The calculations of true and predicted composition were done in parallel during the simulation.

4.0 RESULTS OF THE SIMULATION

4.1 ABILITY TO CONTROL AND PREDICT GLASS COMPOSITION UNDER NORMAL OPERATING CONDITIONS

The mass balance simulation model was exercised many times to investigate the effects of different WLST and FPT sampling strategies on the ability to control and predict the composition of the glass being produced. All of the runs simulated the LFCM process in operation under normal conditions; there were no process upsets other than normal process fluctuations, and there was no bias introduced. The difference between the true composition and the target composition provided a measure of how well the process was controlled. Likewise, the difference between the predicted composition and the true composition provided a measure of how well the glass composition was predicted.

The following sampling strategies were investigated:

- Case 1: One sample and one analysis of both the WLST and the FPT.
- Case 2: One sample and one analysis of the WLST, five samples and five analyses of each sample of the FPT.
- Case 3: Five samples and five analyses of each sample of the WLST, one sample and one analysis of the FPT.
- Case 4: Five samples and five analyses of each sample of both the WLST and the FPT.
- Case 5: A case in which it was assumed that there were no sampling or analytical errors. This is equivalent to taking an infinite number of samples and performing an infinite number of analyses on each sample of both the WLST and the FPT.

For each of these cases, 10 runs were executed. Each of the 10 runs simulated 4,000 hours of operation of the LFCM vitrification system, giving a total of 40,000 simulated hours (about 4.5 years) of operation for each case. In each run, the true and predicted glass compositions were recorded every 20 hours. True and target glass compositions were compared by examining the average absolute difference ($AAD = |true - target|$). The spread of the

absolute differences was examined by obtaining the 95th percentile point of all absolute differences from the simulation (95% of the differences are less than the 95th percentile point). The 95th percentile point can also be expressed as a percentage of the target value. These values are shown in Table 4.1 for each of the constituents and sampling strategies.

The true and predicted glass compositions can be compared in a manner similar to the true and target compositions. The average absolute differences between the true and predicted compositions and the 95th percentile points are presented in Table 4.1. When the 95th percentile point is represented as a percentage of the target value (average true value), one can say that approximately 95% of the differences between true and predicted values are within $\pm X\%$ of the target. The utility of this is that a waste-form producer could place error bands of $\pm X\%$ around the predicted composition values and say that "the true composition of the glass should fall within these error bands 95% of the time."

In general, the difference between the true and predicted compositions is less than $\pm 8\%$ of the target composition. Differences between the true and the target values are generally less than $\pm 10\%$ of the target. The ability to control the glass composition is affected primarily by the WLST sampling strategy, and the ability to predict the glass composition is affected primarily by the FPT sampling strategy. This is exactly what one would expect; since the amount of glass formers added to the FPT is based on the apparent composition in the WLST, and the predicted glass composition is based on the apparent composition in the FPT. In both cases, more samples and analyses lead to better control or prediction.

The effects of different WLST and FPT sampling strategies on true and predicted glass compositions are illustrated graphically in Figures 4.1 through 4.5. These figures contain plots of true and predicted glass composition versus time for a representative run from each of the five sampling strategy cases. Each figure contains a plot of true and predicted mass fraction in the glass of (a) "heat producers" versus time, (b) "other waste" versus time, (c) B_2O_3 versus time, and (d) Na_2O versus time. The plots for SiO_2 and "other glass formers" versus time are not shown because these components exhibited the

TABLE 4.1. Comparisons of True, Predicted, and Target Glass Composition

Constituent	WLST Samples:Analyses	FPT Samples:Analyses	Average Absolute Diff. Between True and Target, TDiff (mass fraction x 10 ³)	95th Percentile of TDiff (mass fraction x 10 ³)	95th Percentile Represented as % of Target	Average Absolute Diff. Between True and Predicted, PDiff (mass fraction x 10 ³)	95th Percentile of PDiff (mass fraction x 10 ³)	95th Percentile Represented as % of Target
Heat	1:1	1:1	0.2869	0.7395	8.8	0.2548	0.65	7.7
	1:1	5:5	0.2939	0.7152	8.5	0.0848	0.22	2.6
	5:5	1:1	0.1294	0.3605	4.3	0.2527	0.64	7.6
	5:5	5:5	0.1331	0.3130	3.7	0.0791	0.21	2.5
	Infinite	Infinite	0.0813	0.2136	2.5	NA	NA	NA
Waste	1:1	1:1	13.592	33.821	11.7	5.903	15.71	5.4
	1:1	5:5	13.495	33.768	11.6	2.270	5.75	2.0
	5:5	1:1	8.961	22.000	7.6	6.583	16.39	5.7
	5:5	5:5	10.193	24.678	8.5	1.942	5.22	1.8
	Infinite	Infinite	8.219	20.603	7.1	NA	NA	NA
B ₂ O ₃	1:1	1:1	1.1695	2.9698	3.3	2.158	5.51	6.0
	1:1	5:5	1.3185	3.4647	3.8	0.739	1.92	2.1
	5:5	1:1	0.8395	2.1253	2.3	2.287	5.57	6.1
	5:5	5:5	0.7913	1.8609	2.0	0.707	1.95	2.1
	Infinite	Infinite	0.7514	1.8444	2.0	NA	NA	NA
SiO ₂	1:1	1:1	10.932	27.864	5.9	6.520	16.37	3.5
	1:1	5:5	10.820	27.246	5.8	2.420	5.89	1.3
	5:5	1:1	6.975	17.332	3.7	6.524	16.21	3.4
	5:5	5:5	8.0059	19.534	4.2	2.190	5.92	1.3
	Infinite	Infinite	6.3293	15.444	3.3	NA	NA	NA
Na ₂ O	1:1	1:1	1.6324	3.9731	5.7	1.957	4.95	7.0
	1:1	5:5	1.6488	4.3420	6.2	0.600	1.49	2.1
	5:5	1:1	1.1006	2.6074	3.7	1.779	4.32	6.2
	5:5	5:5	1.1842	2.9838	4.2	0.553	1.48	2.1
	Infinite	Infinite	1.0657	2.5335	3.6	NA	NA	NA

FIGURE 4.1. Glass Composition versus Time in Case 1 (WLST 1/1, FPT 1/1)

FIGURE 4.2. Glass Composition versus Time in Case 2 (WLST 1/1, FPT 5/5)

FIGURE 4.3. Glass Composition versus Time in Case 3 (WLST 5/5, FPT 1/1)

FIGURE 4.4. Glass Composition versus Time in Case 4 (WLST 5/5, FPT 5/5)

FIGURE 4.5. Glass Composition versus Time in Case 5 (No Sampling Error)

exact same trends as Na_2O . This was expected since Na_2O , SiO_2 and "other glass formers" were always added to the FPT in approximately equal proportions.

Figures 4.1 through 4.5 show how the true and predicted glass compositions fluctuate about the target composition over time. Even in Case 5, which involves no sampling error, it is apparent that process uncertainties such as errors in measuring tank levels and errors in making up and adding glass formers give rise to a certain amount of variability in the glass. The variability in this case represents the process variability mentioned in Section 2.8.

Figure 4.2 shows that when the WLST is sampled/analyzed only once and the FPT is sampled/analyzed many times, glass composition is predicted effectively, but the composition has a high degree of variability. Figure 4.3 on the other hand shows that when the WLST is sampled/analyzed many times and the FPT is sampled/analyzed only once, a glass with a fairly consistent composition is produced, but the composition is poorly predicted. This is consistent with the information presented in Table 4.1. The reason for the very small difference between the true and predicted compositions in Case 5 (Figure 4.5) is that there were no process uncertainties built into the simulation that had a significant effect on composition between the FPT and the melter. Errors in measuring the level in the MFT were included in the simulation, but it was assumed that there were no errors in measuring the cold cap coverage or the glass level in the melter. A direct consequence of this assumption is that essentially all of the difference between the true and predicted glass composition in Figures 4.1 through 4.4 can be attributed to sampling and analytical error associated with measuring the composition in the FPT.

A close look at Figures 4.1 through 4.5 reveals that the mass fraction of "heat producers" and "other waste" often follow similar trends. This is to be expected, since any action taken to adjust the loading of heat producers will have a similar effect on the loading of other waste. Deviations from this behavior are a consequence of batch-to-batch variability in the composition of the waste entering the system.

Examination of Figures 4.1 through 4.5 also reveals a consistent inverse relationship between the mass fraction of other waste and Na_2O versus time. This is a direct result of the way that the control algorithm for addition of

glass formers to the FPT is implemented. The key quantity that drives the control algorithm is the mass ratio of heat producers to total waste in the WLST. When this ratio is high, proportionately more glass formers are added to the waste mixture in the FPT to bring the decay heat loading down. The result is a decreased waste loading and an increased loading of glass-forming constituents (other than B_2O_3 , which is independently controlled). Likewise, when the ratio of heat producers to total waste is low, proportionately fewer glass formers are added to the mixture in the FPT. This results in a higher waste loading and a lower loading of glass formers. Figure 4.6 contains plots of (a) heat to total waste ratio in the WLST versus time and (b) the mass of glass formers added to the FPT versus time for the run shown in Figure 4.4. It can be seen that the mass of glass formers added to the FPT closely follows the trend of the measured heat-to-waste ratio. The glass former curves lag slightly behind the heat-to-waste ratio curve because of the time involved in transferring and evaporating slurry between the WLST and the FPT.

4.2 ABILITY TO DETECT PROCESS UPSETS--QUALITY CONTROL CAPABILITY USING FPT SAMPLES

The ability of the proposed control charts (see Section 2.8) to detect process shifts can be studied by examining the average run length (ARL) of each chart. The ARL is the average number of observations plotted on a control chart after a process upset before detecting an out of control point. The ARL is dependent upon a number of factors: the size of the shift in the process, the number of samples per FPT batch, the number of analyses per sample, and the process variability. The ARL for the simulated LFCM process was examined for three shift sizes, four combinations of the number of samples and analyses per sample from the FPT, and two sampling schemes from the WLST. The examination was accomplished by using a statistical analysis software package to generate 1000 observations for each combination of factors and each constituent. The observations were generated in such a way that they had a first-order autocorrelation structure identical to that of the simulated process data.

A summary of the ARLs for the control chart on the composition of FPT batches is presented in Table 4.2. The sample-to-sample standard deviation and

(a) Ratio of Heat Producers to Total Waste in WLST vs. Time

(b) Mass of Glass Formers Added to FPT vs. Time

FIGURE 4.6. Mass Ratio of Heat Producers to Total Waste in WLST, and Amounts of Glass Formers Added to FPT in Case 4 (WLST 5/5, FPT 5/5)

TABLE 4.2. Average Run Lengths

Component	WLST		Percent Shift ^(a)	Average Run Lengths ^(d)			
	Samples	Analyses		NS ^(b) = 1 NA ^(c) = 1	NS = 1 NA = 3	NS = 3 NA = 1	NS = 3 NA = 3
B ₂ O ₃	1	1	10	>20	>20	>20	>20
B ₂ O ₃	1	1	15	>20	14	7	7
B ₂ O ₃	1	1	25	3	2	2	2
B ₂ O ₃	5	5	10	>20	>20	>20	11
B ₂ O ₃	5	5	15	19	7	3	3
B ₂ O ₃	5	5	25	1	1	1	1
SiO ₂	1	1	10	>20	>20	>20	>20
SiO ₂	1	1	15	>20	>20	>20	18
SiO ₂	1	1	25	8	6	4	5
SiO ₂	5	5	10	>20	>20	>20	>20
SiO ₂	5	5	15	>20	15	9	6
SiO ₂	5	5	25	2	2	2	1
Na ₂ O	1	1	10	>20	>20	>20	>20
Na ₂ O	1	1	15	>20	>20	>20	>20
Na ₂ O	1	1	25	8	6	4	4
Na ₂ O	5	5	10	>20	>20	>20	>20
Na ₂ O	5	5	15	>20	13	8	7
Na ₂ O	5	5	25	2	2	2	2
Heat	1	1	10	>20	>20	>20	>20
Heat	1	1	15	>20	>20	11	7
Heat	1	1	25	4	3	2	2
Heat	5	5	10	>20	>20	>20	>20
Heat	5	5	15	>20	>20	10	7
Heat	5	5	25	4	2	2	1
Waste	1	1	10	>20	>20	>20	>20
Waste	1	1	15	>20	>20	11	7
Waste	1	1	25	4	2	2	2
Waste	5	5	10	>20	>20	>20	>20
Waste	5	5	15	>20	>20	10	8
Waste	5	5	25	4	2	2	1

(a) Percent shift is represented as a percent of the target feed composition.

(b) NS is the number of samples obtained from each FPT batch.

(c) NA is the number of analyses performed per FPT sample.

(d) Large ARL values are not very accurate since this was based on a simulation of only 1000 FPT batches.

the analytical standard deviation were each assumed to be 5% of the target feed composition for the "heat producers" and "other waste" constituents and 4% for the B_2O_3 , SiO_2 and Na_2O constituents. These values are conservative estimates based on data reported in the letter report "Sampling Plan for the WVDP Feed Concentrator Make-Up Tank" (Bowen and Pulsipher 1985, Section 2.5). Table 4.2 can be used to determine the impact of sampling schemes on the ability of the control charts to detect shifts in the process.

An examination of Table 4.2 reveals that 25% shifts in the process average can be detected on a control chart anywhere from one to eight batches after the shift occurs, depending on the sampling scheme. If one is interested in detecting smaller shifts, the number of either samples or analyses must be increased, or variances due to the process, sampling, or analyses must be decreased.

In practice, site-specific estimates of the variance components used in the construction of these control charts would be estimated from previously collected data and/or simulations of the process and used to determine the sampling schemes in the WLST and FPT which produce acceptable ARL values for detecting unacceptable process shifts. If the ARL values are unacceptable for every economically feasible sampling scheme, one must concentrate on eliminating some of the major sources of process, sampling, or analytical variation. This would be done through statistical experimental design and SPC on other steps within the process, on sampling and sample preparation procedures, and/or on analytical procedures.

5.0 DEPENDENCE OF GLASS DISSOLUTION RATE ON GLASS COMPOSITION

It has been long known that glass composition affects its durability to aqueous attack. Establishing this dependence for the purposes of quality control is important since waste form manufacturers have primary control over glass composition. The importance of glass durability is emphasized in Appendix D, where it is shown that in a repository, the release rate of up to 11 radionuclides may be controlled by the rate of glass dissolution.

An approach is presented here for correlating glass dissolution rate and composition. The method is tested on leach rate data for several waste glass compositions in both fresh water and brines. With this information, a preliminary dependence of dissolution rate and composition is determined. Additionally, methods are developed for relating the uncertainty in predicted glass dissolution rate with the uncertainty in predicted composition of waste glass. The limitations of the method, as imposed by the available data on composition versus leach rate, are identified, and recommendations for future efforts are given.

5.1 APPROACH

The approach adopted here is based on the work of Paul (1977), who correlated glass chemical durability with composition via thermodynamic stability of the glass constituents. Later, Plodinec et al. (1983) applied this method to the evaluation of nuclear waste glasses and several simple glasses. Accordingly, glasses are treated as composite solids of individual silicate and/or oxide phases. The free energies of aqueous dissolution reactions are calculated for these phases, providing an indicator of glass durability.

5.2 PROCEDURE

For the present purpose, glass is considered to be composed of silicate oxides, silica, and metal oxides. The usual glass composition (generally reported as weight percent) is converted to mole fraction, and then the distribution of constituents is altered as follows: oxides that exist in pure form as R_2O are assumed to become R_2SiO_3 in the glass, and similarly oxides such as RO

are assumed to become RSiO_3 . Other oxides and silica remain unchanged. This transformation was performed on five proposed waste glasses that have been studied at PNL; their original oxide composition is in Table 5.1, and the adjusted molar composition is in Table 5.2. (some minor constituents were eliminated, and an adjusted mole percent is shown). Several of the glasses differ in the oxidation state of the iron. Glasses 1 and 5 were made under reducing conditions, and the ratio of ferrous to ferric is about 0.3. A corresponding amount of iron has thus been converted to FeSiO_3 . Glass 4 was produced under oxidizing conditions, so the resultant form of iron is assumed to be Fe_2O_3 , which remains as such in the glass. No specific information was available as to how the glasses 2 and 3 were made, so it is assumed that oxidizing conditions prevailed.

The next step is to identify an aqueous reaction for each of the glass constituents. These reactions and their standard free energies at 90°C are defined in Table 5.3 (Paul 1977). Because most of the relevant glass dissolution tests have been done at 90°C , the free energies found in Paul have been extrapolated to this temperature using standard enthalpies and the Van't Hoff equation. It is assumed that the driving force for these individual reactions is determined according to their free energy, which is calculated as follows:

$$G = RT \ln Q + G^\circ \quad (5.1)$$

where $Q = \prod_i a_i \nu_i$ is the ratio of the activities of the products and reactants, where a_i is the activity of a product or reactant, and ν_i is the associated stoichiometric coefficient.

The free energies are to be correlated with glass dissolution rates. Most leach tests are performed in fixed volumes of water, and the dissolution rate generally is found to decrease with time. This trend is associated with "saturation" effects. In a repository, it is expected that slow mass transfer rates away from the waste package will result in similar saturation. Therefore, such leach tests provide useful information about the behavior of glass in repositories. The rates used for correlating with free energies are those obtained at "saturated" or nearly saturated leachate conditions from these static tests.

TABLE 5.1. Simulated Nuclear Waste Glass Compositions (weight percent)

Oxide	1	2	3	4	5(a)
Al ₂ O ₃	4.88	4.3	0	3.31	3.31
B ₂ O ₃	7.12	6.9	9.47	9.96	9.96
BaO	0.11	0.1	0.59	0.06	0.06
CaO	0.97	1.6	2	0.61	0.61
CeO ₂	0.12	0	1.26	0	0
Cr ₂ O ₃	0.14	0	0.44	0.22	0.22
Cs ₂ O	0	0.1	1.1	0.1	0.1
CuO	0.06	0	0	0	0
Fe ₂ O ₃	10.8	11.8	10.3	11.8	9.1
FeO	0	0	0	0	2.4
K ₂ O	0.09	0.2	0	3.51	3.51
La ₂ O ₃	1.1	0	0.56	0	0
Li ₂ O	5.1	4.8	0	3.05	3.05
MgO	0.75	0.6	0	1.31	1.31
MnO ₂	3.3	2.8	0	1.73	1.73
MoO ₃	0	0.1	2.43	0	0
Na ₂ O	10.9	10.8	12.8	11	11
Nd ₂ O ₃	0.6	0.2	4.56	0	0
NiO	0.85	0.8	0.21	0.7	0.7
P ₂ O ₅	0.03	0.3	0.51	2.5	2.5
PbO	0.11	0	0	0	0
RuO ₂	0.1	0	1	0.08	0.08
SiO ₂	51.36	51.7	40	45.2	45.2
SrO	0.03	0	0.4	0.12	0.12
TiO ₂	0	0.2	2.97	0.97	0.97
U ₃ O ₈	0	1.9	0	0.5	0.5
ZnO	0.27	0.1	4.97	0	0
ZrO ₂	1.52	0.9	1.88	3.12	3.12
	100.31	100.2	97.45	99.85	99.55

(a) Glass 5 is the same as glass 4 with a portion of the iron reduced to Fe⁺⁺.

TABLE 5.2. Adjusted Composition of Glasses from Table 5.1 (mole percent)

Oxides	1	2	3	4	5
Al ₂ O ₃	4.67	4.01	0.00	3.34	3.40
B ₂ O ₃	9.98	9.43	15.47	14.71	14.98
CaSiO ₃	1.69	2.71	4.05	1.12	1.14
Fe ₂ O ₃	4.97	7.01	7.32	7.58	5.89
FeSiO ₃	3.03	0.00	0.00	0.00	3.55
K ₂ SiO ₃	0.09	0.20	0.00	3.83	3.90
Li ₂ SiO ₃	16.58	15.21	0.00	10.45	10.64
MgSiO ₃	1.81	1.42	0.00	3.34	3.40
MnSiO ₃	3.70	3.06	0.00	2.04	2.08
Na ₂ SiO ₃	14.16	16.56	23.47	18.24	18.57
SiO ₂	39.00	40.03	38.53	34.09	31.18
TiO ₂	0.00	0.24	4.22	1.25	1.27
ZnSiO ₃	0.32	0.12	6.94	0.00	0.00
	100.00	100.00	100.00	100.00	100.00

TABLE 5.3 Assumed Hydration Reactions and Their Free Energies

Reaction	Standard Free Energy at 90°C, Kcal/Mole
Al ₂ O ₃ + H ₂ O → 2Al(OH) ₃	+4
B ₂ O ₃ + 3H ₂ O → 2H ₃ BO ₃	-8.2
CaSiO ₃ + 2H ⁺ → H ₂ SiO ₃ + Ca ⁺⁺	-15.6
Fe ₂ O ₃ + 3H ₂ O → 2Fe(OH) ₃	+17.02
FeSiO ₃ + 2H ⁺ → H ₂ SiO ₃ + Fe ⁺⁺	-14.5
K ₂ SiO ₃ + 2H ⁺ → H ₂ SiO ₃ + 2K ⁺	-41.7
Li ₂ SiO ₃ + 2H ⁺ → H ₂ SiO ₃ + 2Li ⁺	-23.7
MgSiO ₃ + 2H ⁺ → H ₂ SiO ₃ + Mg ⁺⁺	-12.2
MnSiO ₃ + 2H ⁺ → H ₂ SiO ₃ + Mn ⁺⁺	-11.8
Na ₂ SiO ₃ + 2H ⁺ → H ₂ SiO ₃ + 2Na ⁺	-27.8
SiO ₂ + H ₂ O → H ₂ SiO ₃	+9.2
TiO ₂ + H ₂ O → TiO(OH) ₂	+16.0
ZnSiO ₃ + 2H ⁺ → H ₂ SiO ₃ + Zn ⁺⁺	-15.2

Grambow (1985) attributes this final rate to the residual affinity of the glass to dissolve in aqueous solution. Final dissolution rates for the various glasses are given in Table 5.4; these rates are derived from changes in the concentration of soluble species dissolved from the glass, such as sodium, boron, and lithium. Glasses 2 and 3 were dissolved in saturated brine while glasses 1, 4, and 5 were dissolved in a starting liquid of deionized water. The static test method was used at a temperature of 90°C. The rate data in Table 5.4 were obtained from experiments performed at PNL. The data are preliminary and should be used with caution.

The solution composition associated with these rates is also shown, thus permitting calculation of the activity ratio in Equation 5.1 (unit activity coefficients are assumed for dissolved species). Aqueous metal species are assumed to exist as single or double charged metal cations. Dissolved silicon is assumed to be either H_2SiO_3 or HSiO_3^- ; similarly, dissolved boron can be either H_3BO_3 or H_2BO_3^- (depending on pH, see below). Dissolved iron is rarely found when analyzing leachates, because of the low solubility of iron species. The concentration of ferrous ion for tests with glasses containing FeSiO_3 was arbitrarily set at 0.1 ppm. In the tests with deionized water as starting leachants, the final concentrations of boron, silicon, and calcium were

TABLE 5.4. Dissolution Rates and Free Energies for Waste Glasses

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Dissolution Rate ^(a) 90°C, g-glass/m ² d	0.016	0.01	0.036	0.035	0.25
Free Energy of Glass/Water System at 90°C (G), kcal/mole	0.26	0.5	0.9	-1.9	-1.8
Standard Free Energy of Glass at 90°C (G°), kcal/mole	-5.5	-4.9	-4	-6.4	-7.7

(a) Preliminary data obtained at PNL.

directly measured. The concentrations of lithium, sodium, potassium, manganese, and zinc were determined by assuming congruent release with dissolved boron. In the brine solutions, the concentrations of lithium, boron, and silicon were measured and the concentrations of manganese and zinc were inferred from boron. The quantities of dissolved lithium, sodium, potassium, and magnesium were specified by the initial brine composition.

The solution pH affects the concentration of dissolved silicic and boric acids according to the following relations:

$$C_{H_2SiO_3} = (C_H + C_{Si}) / (K_1 + C_H) \quad (5.2)$$

$$C_{H_3BO_3} = (C_H + C_B) / (K_1 + C_H) \quad (5.3)$$

where C refers to molar concentrations and K_1 is the first ionization constant for each of the acids. For silicic acid, K_1 is 10^{-10} ; and for boric acid, K_1 is $10^{-9.216}$ (Paul and Cooke 1978). The amount of dissolved silica is important because it affects many of the reactions in Table 5.3.

With the solution composition data and the standard free energies, the free energy of individual reactions in the specific aqueous environment can be calculated. As a measure of reactivity in aqueous solutions, the overall free energy of the glasses is calculated on the basis of composition:

$$G = \sum n_i (RT \ln(Q_i) + G_i^0) \quad (5.4)$$

where n_i is the mole fraction of glass constituents. The result is shown in Table 5.4, where Q_i has been estimated from the estimated solution concentrations listed in Table 5.5. Grambow (1985) reported that dissolution rate should depend on free energy according to

$$\ln(\text{Rate}) = A' - B G \quad (5.5)$$

TABLE 5.5. Solution Compositions (M) After Dissolution of Waste Glasses

Species	1	2	3	4	5
Ca ⁺⁺	2×10^{-5}	4×10^{-2}	4×10^{-2}	2×10^{-5}	2×10^{-5}
Fe ⁺⁺	2×10^{-6}	0	0	2×10^{-6}	2×10^{-6}
K ⁺	2×10^{-5}	1×10^{-3}	1×10^{-3}	7×10^{-4}	7×10^{-4}
Li ⁺	3×10^{-3}	30	0	2×10^{-3}	2×10^{-3}
Mg ⁺⁺	2×10^{-4}	6×10^{-3}	6×10^{-3}	3×10^{-4}	3×10^{-4}
Mn ⁺⁺	4×10^{-4}	5×10^{-4}	0	2×10^{-4}	2×10^{-3}
Na ⁺	4×10^{-3}	5.2	5.2	4×10^{-3}	4×10^{-3}
Zn ⁺	3×10^{-5}	2×10^{-6}	2×10^{-6}	0	0
H ₂ SiO ₃	2×10^{-3}	5×10^{-4}	2×10^{-3}	1×10^{-3}	1×10^{-3}
H ₃ BO ₄	4×10^{-4}	2×10^{-3}	7×10^{-3}	4×10^{-4}	4×10^{-3}
H ⁺	1×10^{-10}	1×10^{-9}	1×10^{-9}	1×10^{-10}	1×10^{-10}

where A' and B are constants at a fixed temperature. Following Grambow, a plot of log rate versus G is shown in Figure 5.1. Only a crude trend is obeyed, where the more stable glasses (glasses 1 and 2) exhibit the lower dissolution rates.

5.3 APPROXIMATE TREATMENT OF AQUEOUS CHEMISTRY

Part of the uncertainty in developing this correlation is the dependence of G_i on solution chemistry. Many simplifying assumptions had to be made in order to carry out the calculation. The free-energy term in Equation 5.2 involving activities of reactants and products should be regarded as speculative for several reasons. The solution composition information in Table 5.5 has in some cases been estimated. The pH-dependent speciation of many of the metals has not been rigorously treated. Activity coefficients have been set at 1 (in brines, this is known to be incorrect). Also not taken into account are the many possible mineral phases that can form, such as alumino-silicates and iron silicates. To track these various interactions, a geochemical code such as PHREEQE or EQ3/6 is needed, but such an endeavor is beyond the scope of the current purpose.

FIGURE 5.1. Dependence of Final Dissolution Rate at 90°C on Free Energy of Hydration

As an alternative to calculating the activities of aqueous species, the correlation was attempted using only the standard free energies in Table 5.2. The standard free energies for the glasses, calculated without the activity term, are shown in Table 5.3, and a plot according to dissolution rate is given in Figure 5.2. The data are found to correlate much better when compared to the plot of Figure 5.1. This approach is seemingly at odds with the dependence suggested by Equation 5.5, where the solution activity contribution to the total free energy is included. However, rearrangement of Equation 5.5 is possible such that the dependent variable is only the standard free energy term. Expanding Equation 5.5 with Equation 5.4 results in

$$\ln(\text{Rate}) = A' - B n_i RT \ln(Q_i) - B G^\circ \quad (5.6)$$

FIGURE 5.2. Dependence of Final Dissolution Rate at 90°C on Standard Free Energy of Hydration

Combining the terms A' and $B \sum_i n_i RT \ln(Q_i)$ into a new "constant" A results in

$$\ln(\text{Rate}) = A - B G^\circ \quad (5.7)$$

where G° is the standard free energy of hydration of the glass and is given by $\sum_i n_i G_i^\circ$. By combining the solution activity term into a constant, Equation 5.7 implies that the free energy contribution of the aqueous-solution activities for all glasses is the same. This is not rigorously correct; however, such an approximation may be reasonable, considering that many of the dissolved species are at their solubility limits. Evidently, making this gross assumption about the solutions is better than attempting to calculate solution activities with the available information, as shown by the improvement in the correlation from

Figure 5.1 to 5.2. Thus a potential advantage in this simplified approach is identified: errors or biases introduced by assumptions about activities and speciation and by estimates on solution composition are avoided.

In Figure 5.2, glass 3 is found to deviate from the general trend exhibited by the more recent waste glass compositions. It has the most positive value for G° , yet exhibits a higher glass dissolution rate than would be expected. The reason could be the high degree of phase separation in this glass, where the borate-rich phase is unstable against aqueous attack. For the present purposes, the glass 3 datum will be ignored. Putting a straight line through the four data according to Equation 5.7 results in the following values for the parameters A and B:

$$A = -10.43 \pm 0.8$$

$$B = 1.15 \pm 0.13$$

where the error terms on the parameters have been determined by least square regression. This regression analysis is subject to uncertainty; there are two adjustable parameters but only four available observations. Equation 5.7, with these coefficients, is thus the resulting empirical correlation for the composition dependence of the final dissolution rate of nuclear waste glasses at 90°C.

5.4 SENSITIVITY OF DISSOLUTION RATE TO VARIATIONS IN COMPOSITION

With the correlation above, the glass composition can now be related to dissolution rate. The overall objective, however, is to understand how changes in composition (due to vitrification process variations) will affect this dissolution rate. Uncertainties associated with the vitrification process are to be propagated to a variation in leach rate of the glass. Using statistical propagation of error methods, the error in Equation 5.7 is given by the following relation:

$$\sigma_{\ln R} = \left[\left(\frac{\partial \ln R}{\partial A} \sigma_A \right)^2 + \left(\frac{\partial \ln R}{\partial B} \sigma_B \right)^2 + \left(\frac{\partial \ln R}{\partial G} \sigma_G \right)^2 + 2 \operatorname{cov}(A, B) \frac{\partial \ln R}{\partial A} \frac{\partial \ln R}{\partial B} \right]^{1/2} \quad (5.8)$$

where σ_A^2 , σ_B^2 and σ_G^2 are the variances of A, B, and G° , respectively, and $\text{cov}(A,B)$ is the covariance of A with B. Carrying out the differentiation in Equation 5.8 yields

$$\sigma_R = [\sigma_A^2 - 2G \text{cov}(A,B) + (G^\circ \sigma_B)^2 + (B \sigma_G)^2]^{1/2} \quad (5.9)$$

The error in the free energy σ_G depends on errors in individual glass component free energies, and also on errors in composition. The assumptions that the component free energies are known exactly and, further, that mole fractions can be varied independently result in the following simplified relation for σ_G :

$$\sigma_G = [\sum (G_i^\circ \sigma_{ni})^2]^{1/2} \quad (5.10)$$

where σ_{ni} is the error in mole fraction of individual components and we assume for convenience that the component compositions are not correlated. In reality, the mole fractions of the components will be correlated to some extent because 1) certain components vary in proportion to each other and 2) as the mole fraction of one component increases, the mole fractions of one or more other components will necessarily decrease. If it is assumed that all mole fractions of glass constituents are known to within the same fractional limit f , then substituting $\sigma_{ni} = f n_i$ into Equation 5.10 results in

$$\sigma_G = f [\sum (n_i G_i^\circ)^2]^{1/2} \quad (5.11)$$

In Equation 5.11, it is implied that the uncertainty in the value of G° is directly proportional to f . This situation will not always occur; the value of G° may or may not be sensitive to changes in composition, depending on which components are changing. Ideally, the value of G° should be calculated for each composition that exists in the melter. In the future, this will be done in the simulation, with G° being calculated each time the composition of the glass is written to an output file. This will enable a direct determination of the uncertainty in the value of G° . For now, we use Equation 5.11 to predict the dependence of σ_G on f .

Of interest in this analysis is the sensitivity of the error term for the predicted glass dissolution rate (Equation 5.8) on the composition error factor f . To carry out the analysis numerically, a value of $G^\circ = -6.39$ kcal/mole is selected, corresponding to glass 4. Using the composition and standard free energies from Tables 5.2 and 5.3, the term $[\sum(n_i G_i^\circ)^2]^{1/2}$ in Equation 5.11 becomes 6.89 kcal/mole. The regression analysis done above resulted in values of $\sigma_A = 0.8$, $\sigma_B = 0.13$, and $\text{cov}(A,B) = 0.102$. Equation 5.8 becomes

$$\sigma_{\ln R} = (0.026 + 62.8 f^2)^{1/2} \quad (5.12)$$

Using Equation 5.12, $\sigma_{\ln R}$ can be calculated for different values of f . The values of $\sigma_{\ln R}$, in turn, can be used to calculate upper and lower error bounds for the dissolution rate, R , as a function of f . This was done by adding and subtracting the value of $\sigma_{\ln R}$ from $\ln R$, which was -3.352 in all cases (glass 4), and then taking the antilog of the result. Table 5.6 shows the results of this analysis for glass 4. The error bounds in Table 5.6 should not be interpreted as confidence limits. These values qualitatively show the impact that f has on the uncertainty in dissolution rate, but they do not correspond to a fixed level of confidence.

From Table 5.6, it is apparent that there is a base level of uncertainty associated with the glass dissolution rate, even when the uncertainty in composition is assumed to be zero. The uncertainty in glass dissolution rate does not increase significantly until the value of f becomes greater than 0.02. The results of the process simulation described in Section 4.0 indicate that inherent process variations (excluding upsets) would result in compositional uncertainties on the order of 2% to 11.5% (f values on the order of 0.02 to 0.115) if the assumed standard deviations for stochastic process parameters are correct. Therefore, if it is important to minimize the uncertainty in glass dissolution rate, it would be worthwhile to control the process to the 2% fluctuation level rather than to higher fluctuation levels, which in turn would require more extensive sampling and analyses of the waste. It should be

TABLE 5.6. Upper and Lower Error Bounds in the Dissolution Rate of Glass 4 (R) as a Function of Uncertainty in Composition (f)

<u>f</u>	<u>$\sigma_{\ln R}$</u>	<u>Lower Bound^(a)</u>	<u>Upper Bound^(a)</u>
0	0.161	0.030	0.041
0.01	0.180	0.029	0.042
0.02	0.226	0.028	0.044
0.03	0.287	0.026	0.047
0.05	0.428	0.023	0.054
0.10	0.809	0.016	0.079
0.20	1.593	0.007	0.172

(a) The predicted value of R is 0.035 g-glass/m²d (see Table 5.4).

recognized, however, that the glass dissolution rate may be sufficiently low that even with a large amount of uncertainty in the rate it is extremely unlikely that radionuclide release rates will exceed regulatory criteria. If this is the case, it will not be strictly necessary to control the process to the 2% fluctuation level.

The uncertainty in the predicted dissolution rate can result from three factors: 1) uncertainties in free energies, 2) uncertainties in experimental measurements on dissolution rate, or 3) a poor model for predicting the relationship between composition and dissolution rate. In Figure 5.2, the error due to factor 3 could be reduced if a parabola were used to fit the data. However, such a mathematical exercise is not justified. It would be a deviation from the semitheoretical approach implicit in using a straight line; also, the magnitude of the uncertainty due to factors 1 and 2 is unknown.

5.5 NEED FOR ADDITIONAL DATA

The analysis has shown how composition and dissolution rate can be correlated, and how uncertainties in composition due to the vitrification process can influence dissolution rate. The data used to demonstrate the methodology were taken from previously conducted experiments that were not aimed at this

purpose, so the numerical results are not applicable to any specific vitrification process. The analysis does indicate that consideration of the free energies of hydration of glass constituents may provide a reasonable framework for correlating glass dissolution rate and composition. Future efforts to improve and validate this approach are needed. The following work is indicated:

- Leach tests should emphasize determination of glass dissolution rate in solutions saturated with dissolution products.
- Tests are needed on a range of glass compositions (about a target composition).
- More precise information on solution activities is needed so that the solution portion of the free-energy equation can be used.

6.0 DEPENDENCE OF RADIONUCLIDE RELEASE RATE ON GLASS DISSOLUTION RATE

Contact of disposed vitrified waste with groundwater is the primary mechanism for release of radionuclides. Because glass dissolves slowly, this process is expected to ensure slow release of radionuclides. The low solubility of many radionuclides, however, may provide a more restrictive limit for release. The analysis performed here provides an indication of which radionuclides are expected to be controlled by glass dissolution rate, and which are expected to be controlled by solubility.

6.1 APPROXIMATE ANALYSIS OF MASS TRANSFER

It is assumed that the waste solid is a sphere embedded in an infinite porous medium, and that there is no convection. The flux at the surface of the solid is given by the glass dissolution rate J_0 (g-glass/m²d) times the fractional loading of a radionuclide f (curies/g-glass). At steady state, the concentration profile is given by

$$C \text{ (curies/m}^3\text{)} = \alpha + \beta/r \quad (6.1)$$

where r is radial position away from the sphere, and α and β are constants to be determined by boundary conditions (Carslaw and Jaeger 1959). The concentration far away from the waste is zero, so $\alpha = 0$. Radionuclides whose release is controlled by diffusion will be at their solubility limits at the surface of the glass, so the constant β is given by

$$\beta = r_0 C_s \quad (6.2)$$

where C_s is the radionuclide solubility limit. This gives the solution for C :

$$C = r_0 C_s / r \quad (6.3)$$

The diffusive flux is given by

$$J_D = -DdC/dr \text{ (} r = r_0 \text{)} = DC_s/r_0 \quad (6.4)$$

where D is the diffusivity in the porous medium.

6.2 GLASS DISSOLUTION CONTROL

Radionuclides with high solubility will be limited only by the kinetics of glass dissolution. If glass dissolves at a constant rate J_0 (g-glass/m²d), then the associated radionuclide release J_K (curies/m²d) is given by

$$J_K = fJ_0 \quad (6.5)$$

where f is the radionuclide loading in the glass (curies/g-glass).

6.3 EFFECT OF ESTIMATED RADIONUCLIDE SOLUBILITIES

The criteria for determining whether a given radionuclide is going to be controlled by solubility limits or the glass dissolution rate is the ratio of the kinetic flux J_K to the diffusive flux J_D . If J_K/J_D is less than 1, then glass dissolution controls the release of radionuclides; and if the ratio is greater than 1, then release is under solubility control. The radionuclide solubility is related to the corresponding element solubility (C_e , g/m³) according to

$$C_s = C_e I/M \quad (6.6)$$

where I is the inventory of the radionuclide in the waste (curies/MTU) and M is the inventory of the corresponding element in the waste (g/MTU). Also, the factor f in Equation 6.5 is equivalent to

$$f = I * L \quad (6.7)$$

where L is the waste loading in the glass (MTU/g-glass). If Equation 6.7 is inserted into Equation 6.5 and divided by Equation 6.4, the resulting ratio is:

$$J_K/J_D = LMJ_0 r_0 / (C_e D) \quad (6.8)$$

As noted in Section 5.0, an approximate steady-state glass dissolution rate is $J_0 = 0.04 \text{ g/m}^2\text{d}$. For commercial waste glass, the waste loading L is expected to be about $7 \times 10^{-6} \text{ MTU/g-glass}$, according to the Environmental Impact Statement for commercial waste (DOE 1980). A high-level waste inventory is given by the same reference, and M is thus specified for various elements (inventory at 1000 years after closure is used). The diffusivity D is taken to be a representative free-liquid value of $10^{-5} \text{ cm}^2/\text{s}$ multiplied by a representative host rock porosity of 0.01. A radius r_0 of 0.2 m is used, which is larger than the expected diameter of a cylinder of waste glass because the assumed geometry is a sphere. Generic values of radionuclide element solubility C_e were found in the literature, and are given in Table 6.1. The solubility data are estimated for both reducing and oxidizing conditions, with pH values thought to be representative of repository environments. Solubility data were not available for some elements that are generally considered to have relatively high solubility. It is assumed that these elements and their radionuclide isotopes will be controlled by the glass dissolution rate.

Substituting the aforementioned information into Equation 6.8 results in values for J_K/J_0 . These are presented in Table 6.2, where both sets of solubility data are utilized. Owing to the uncertainties in the estimates used here, ratios should be at least 10 before one concludes that solubility is controlling. As expected, the low solubilities in Table 6.1 yield ratios that are generally much larger than 1, indicating solubility control.

Solubilities in oxidizing environments are generally higher than in reducing environments. Therefore, J_K/J_0 values are generally smaller in the oxidizing case than in the reducing case. Radionuclides with low J_K/J_0 values include isotopes of technetium, cesium, actinium, radium, lead, thorium, protactinium, neptunium, and nickel. Overall, there are about 11 radionuclides that could potentially be controlled by glass dissolution rate.

As stated earlier, this analysis was done under the assumption that there is no convective flux around the waste package. If convection becomes important, it is possible that more radionuclides could be controlled by the glass dissolution rate. However, it is widely believed that the convective flux in most geologic repository scenarios will be negligible.

TABLE 6.1. Solubilities Used in Analysis

Element	pH 9-10, Reducing, g/L	Reference	pH 7, Oxidizing, g/L	Reference
Ni	3×10^{-7}	1	1×10^{-3}	1
Np	3×10^{-10}	2	5×10^{-3}	3
U	1×10^{-8}	4	4×10^{-4}	5
Pu	6×10^{-10}	6	5×10^{-5}	7,8
Th	4×10^{-7}	9	1×10^{-6}	9
Am	1×10^{-10}	10	1×10^{-9}	10
Cm	1×10^{-10}	10	1×10^{-9}	10
Zr	1×10^{-7}	11	1×10^{-7}	11
Sn	1×10^{-7}	11	1×10^{-7}	11
Ra	6×10^{-4}	11	high	11
Pb	1×10^{-4}	11	high	11
Se	1×10^{-6}	11	1×10^{-6}	11
Pd	2×10^{-8}	12	2×10^{-8}	12
Tc	1×10^{-12}	12	high	11

Key to References:

- 1 Martel and Smith 1977
- 2 Rai and Ryan 1984
- 3 Strickert, Rai and Fulton 1984
- 4 Fuger and Oetting 1976
- 5 Thompson et al. 1984
- 6 Rai 1984
- 7 Rai, Serne and Moore 1980
- 8 Rai and Swanson 1981
- 9 Ryan and Rai 1984
- 10 Rai et al. 1981
- 11 National Academy of Sciences 1983
- 12 Early et al. 1982

TABLE 6.2. Ratio of Kinetic to Diffusive Mass Flux for Various Radionuclides

Radionuclide	Oxidizing	Reducing
⁵⁹ Ni	1	8×10^3
⁶³ Ni	1	8×10^3
⁷⁹ Se	3×10^3	3×10^3
⁹³ Zr	2×10^6	2×10^6
⁹⁹ Tc	--(a)	5×10^{10}
¹⁰⁷ Pd	4×10^6	5×10^6
¹²⁶ Sn	2×10^5	2×10^5
¹³⁵ Cs	--(a)	--(a)
¹⁵¹ Sm	2×10^5	3×10^5
²⁴⁵ Cm	7×10^5	7×10^6
²⁴³ Am	2×10^7	2×10^8
²⁴² Am	2×10^7	2×10^8
²⁴¹ Am	2×10^7	2×10^8
²⁴² Pu	185	2×10^7
²⁴⁰ Pu	185	2×10^7
²³⁹ Pu	185	2×10^7
²³⁸ Pu	185	2×10^7
²³⁷ Np	9	2×10^8
²³⁸ U	150	2×10^7
²³⁶ U	150	2×10^7
²³⁵ U	150	2×10^7
²³⁴ U	150	2×10^7
²³³ U	150	2×10^7
²³¹ Pa	0.1	0.09
²³⁰ Th	1	3.45
²²⁹ Th	1	3.45
²²⁷ Ac	--(a)	--(a)
²²⁶ Ra	--(a)	--(a)
²¹⁰ Pb	0.002	0.002

(a) Solubility presumed to be high such that radionuclide is controlled by glass dissolution rate.

7.0 CONCLUSIONS

Methods for controlling and predicting the composition of high-level nuclear waste glass produced in an LFCM process were investigated by simulating process operations. A control algorithm was developed in which upstream sampling of the waste was used to determine the amounts of glass-forming compounds to add to the waste in order to adjust the decay heat loading and boron loading in the glass to desired levels. Prediction of glass composition was based on samples taken of the melter feed (the combined waste and glass former mixture).

The simulations showed the extent to which the glass composition could be 1) better controlled when more samples and more analyses were taken of the waste and 2) better predicted when more samples and more analyses were taken of the feed. The absolute differences between the true and target glass compositions suggested that the composition could be controlled to within 2% to 11.5% of the target composition, depending on the strategy for sampling and analyzing the waste. The absolute differences between the predicted and the true compositions were used to calculate upper and lower confidence limits associated with the predicted composition. These limits were narrower when more samples and more analyses were taken of the feed. The limits ranged from 1.3% to 7.7% (of the target composition), depending on the feed sampling and analytical strategy. The simulation of real processes should be a useful tool for comparing the costs, risks, and benefits associated with different sampling and analytical strategies, provided that sampling and analytical errors and other process uncertainties can be adequately characterized. Sensitivities of the true and predicted glass composition to uncertainties in the magnitude of these errors could also be investigated.

Process control charting limits were established for the boron concentration in the feed. Fluctuations of sampled boron concentration falling within these control limits are considered to be normal; when the concentration falls outside the limits, it is an indication that the process is out of control. The control limits are narrower when more samples and analyses of either the waste or feed are taken, because the uncertainty associated with estimates of waste or feed composition is then reduced.

It was found that a process upset (step change) of 10% from the mean feed composition could not be detected until after 20 batches of feed had been processed (this was true in all cases that were analyzed except for one involving the largest number of samples and analyses of both the waste and the feed, and even in this case the upset could not be detected until after 10 batches of feed). This result suggests that if a process upset of 10% or less is considered important, process control charting should be implemented on elements of the process other than just the feed composition. Control charting on other process measurements would 1) lower the inherent process variability and 2) enable the detection of whatever is causing the upset (perhaps a faulty level measurement, or a biased analysis of glass former composition) at a much earlier time.

A correlation was developed that provides a link between glass composition fluctuations, which are expected from the LFCM process, and variations in the glass dissolution rate. The available data reveal a large uncertainty in the predicted rate, even when the uncertainty in the glass composition is assumed to be zero. In order to better associate process-related composition variations with durability, therefore, more information about glass dissolution rates under repository-relevant conditions is needed. The uncertainty in the glass dissolution rate is increased significantly when the uncertainty in the composition of the glass exceeds 2%. Therefore, if it is important to minimize the uncertainty in glass dissolution rate, there is an incentive to control the process to this 2% level of uncertainty, given the assumptions used in the process simulation. It should be recognized, however, that the glass dissolution rate may be sufficiently low that even with a large amount of uncertainty in the rate it is extremely unlikely that radionuclide release rates will exceed regulatory criteria. If this is the case, it will not be strictly necessary to control the process to the 2% fluctuation level.

In a repository, release from vitrified waste will be controlled either by diffusion of solubility-limited species or by the kinetics of glass dissolution. An analysis was performed comparing these two processes. Low solubility assures diffusion control in most cases; however, the rate of dissolution of the glass is expected to control up to 11 radionuclides. The analysis is not

specific to a particular repository; still, it emphasizes the need for understanding how product variations inherent in the LFCM process are related to variations in glass durability.

The analyses performed for this report will eventually be expanded to provide a more complete demonstration of waste form qualification. Based on the results presented here, the following recommendations are made for future work:

- Process control charts should be incorporated directly into the simulation model, and abnormal process upsets should be simulated so that the utility of the process control charts can be demonstrated.
- Process control charting on a number of process parameters (e.g., tank levels, glass former additions) should be considered so that process upsets can be detected more quickly than simply by control charting the feed composition.
- Strategies for taking corrective action when the process is considered to be out of control should be investigated and ultimately simulated.
- The standard energy of hydration, G° , of the glass should be calculated directly in the simulation model for each batch of glass produced. This would provide a more direct measure of the uncertainty in G° , and hence in glass dissolution rate, than is currently provided.

In addition to the above items, more data are needed on the magnitudes of the uncertainties assumed to characterize the process and on the dissolution rates of glasses of various compositions. Also, the validity and impact of the assumptions made in this report should be examined in greater detail.

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APPENDIX A

MASS BALANCE EQUATIONS FOR SIMULATION MODEL

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MASS BALANCE EQUATIONS FOR SIMULATION MODEL

Waste Receiving and LAG Storage Tank (WLST)

$$\begin{aligned}D(1) &= S(82) - S(83) \\D(2) &= S(139)*S(82) - S(97)*S(83) \\D(3) &= S(140)*S(82) - S(98)*S(83) \\D(4) &= 0.0 \\D(5) &= 0.0 \\D(6) &= 0.0 \\D(7) &= 0.0 \\S(67) &= S(1) - S(2) - S(3) \\S(97) &= S(2)/S(1) \\S(98) &= S(3)/S(1) \\S(103) &= 1.0 - S(97) - S(98)\end{aligned}$$

Waste Concentration Tank (WCT)

$$\begin{aligned}D(8) &= S(83) - S(84) - S(85) \\D(9) &= S(97)*S(83) - S(104)*S(85) \\D(10) &= S(98)*S(83) - S(105)*S(85) \\D(11) &= 0.0 \\D(12) &= 0.0 \\D(13) &= 0.0 \\D(14) &= 0.0 \\S(68) &= S(8) - S(9) - S(10) \\S(104) &= S(9)/S(8) \\S(105) &= S(10)/S(8) \\S(110) &= 1.0 - S(104) - S(105)\end{aligned}$$

Feed Preparation Tank (FPT)

$$\begin{aligned}D(15) &= S(85) + S(86) + S(87) - S(88) - S(89) \\D(16) &= S(104)*S(85) - S(111)*S(89) \\D(17) &= S(105)*S(85) - S(112)*S(89) \\D(18) &= S(142)*S(86) + S(147)*S(87) - S(113)*S(89) \\D(19) &= S(143)*S(86) + S(148)*S(87) - S(114)*S(89) \\D(20) &= S(144)*S(86) + S(149)*S(87) - S(115)*S(89) \\D(21) &= S(145)*S(86) + S(150)*S(87) - S(116)*S(89) \\S(69) &= S(15)-S(16)-S(17)-S(18)-S(19)-S(20)-S(21) \\S(111) &= S(16)/S(15) \\S(112) &= S(17)/S(15) \\S(113) &= S(18)/S(15) \\S(114) &= S(19)/S(15) \\S(115) &= S(20)/S(15) \\S(116) &= S(21)/S(15) \\S(117) &= 1.0-S(111)-S(112)-S(113)-S(114)-S(115)-S(116)\end{aligned}$$

Melter Feed Tank (MFT)

$$\begin{aligned}D(22) &= S(89) - S(90) \\D(23) &= S(111)*S(89) - S(118)*S(90) \\D(24) &= S(112)*S(89) - S(119)*S(90) \\D(25) &= S(113)*S(89) - S(120)*S(90) \\D(26) &= S(114)*S(89) - S(121)*S(90) \\D(27) &= S(115)*S(89) - S(122)*S(90) \\D(28) &= S(116)*S(89) - S(123)*S(90) \\S(70) &= S(22)-S(23)-S(24)-S(25)-S(26)-S(27)-S(28) \\S(118) &= S(23)/S(22) \\S(119) &= S(24)/S(22) \\S(120) &= S(25)/S(22) \\S(121) &= S(26)/S(22) \\S(122) &= S(27)/S(22) \\S(123) &= S(28)/S(22) \\S(124) &= 1.0-S(118)-S(119)-S(120)-S(121)-S(122)-S(123)\end{aligned}$$

Melter Cold Cap

$D(29) = S(90) - S(91) - S(93)$
 $D(30) = S(118)*S(90) - S(125)*S(91)$
 $D(31) = S(119)*S(90) - S(126)*S(91)$
 $D(32) = S(120)*S(90) - S(127)*S(91)$
 $D(33) = S(121)*S(90) - S(128)*S(91)$
 $D(34) = S(122)*S(90) - S(129)*S(91)$
 $S(71) = S(29)-S(30)-S(31)-S(32)-S(33)-S(34)$
 $S(72) = 0.0$
 $S(91) = 1.7836*S(128)*S(29)$
 $S(93) = S(124)*S(90)$
 $S(125) = S(30)/S(29)$
 $S(126) = S(31)/S(29)$
 $S(127) = S(32)/S(29)$
 $S(128) = S(33)/S(29)$
 $S(129) = S(34)/S(29)$
 $S(130) = 1.0-S(125)-S(126)-S(127)-S(128)-S(129)$
 $S(131) = 0.0$

Glass in Melter

$D(35) = S(91) - S(92)$
 $D(36) = S(125)*S(91) - S(132)*S(92)$
 $D(37) = S(126)*S(91) - S(133)*S(92)$
 $D(38) = S(127)*S(91) - S(134)*S(92)$
 $D(39) = S(128)*S(91) - S(135)*S(92)$
 $D(40) = S(129)*S(91) - S(136)*S(92)$
 $D(66) = S(90) - S(92) - S(93)$
 $S(73) = S(35)-S(36)-S(37)-S(38)-S(39)-S(40)$
 $S(74) = 0.0$
 $S(132) = S(36)/S(35)$
 $S(133) = S(37)/S(35)$
 $S(134) = S(38)/S(35)$
 $S(135) = S(39)/S(35)$
 $S(136) = S(40)/S(35)$
 $S(137) = 1.0-S(132)-S(133)-S(134)-S(135)-S(136)$
 $S(138) = 0.0$

Predicted Melter Feed Tank (MFT)

$$\begin{aligned}D(41) &= S(94) - S(90) \\D(42) &= S(159)*S(94) - S(166)*S(90) \\D(43) &= S(160)*S(94) - S(167)*S(90) \\D(44) &= S(161)*S(94) - S(168)*S(90) \\D(45) &= S(162)*S(94) - S(169)*S(90) \\D(46) &= S(163)*S(94) - S(170)*S(90) \\D(47) &= S(164)*S(94) - S(171)*S(90) \\S(75) &= S(41)-S(42)-S(43)-S(44)-S(45)-S(46)-S(47) \\S(166) &= S(42)/S(41) \\S(167) &= S(43)/S(41) \\S(168) &= S(44)/S(41) \\S(169) &= S(45)/S(41) \\S(170) &= S(46)/S(41) \\S(171) &= S(47)/S(41) \\S(172) &= 1.0-S(166)-S(167)-S(168)-S(169)-S(170)-S(171)\end{aligned}$$

Predicted Melter Cold Cap

$$\begin{aligned}D(48) &= S(90) - S(95) - S(96) \\D(49) &= S(166)*S(90) - S(173)*S(95) \\D(50) &= S(167)*S(90) - S(174)*S(95) \\D(51) &= S(168)*S(90) - S(175)*S(95) \\D(52) &= S(169)*S(90) - S(176)*S(95) \\D(53) &= S(170)*S(90) - S(177)*S(95) \\S(76) &= S(48)-S(49)-S(50)-S(51)-S(52)-S(53) \\S(77) &= 0.0 \\S(95) &= 1.7836*S(176)*S(48) \\S(96) &= S(172)*S(90) \\S(173) &= S(49)/S(48) \\S(174) &= S(50)/S(48) \\S(175) &= S(51)/S(48) \\S(176) &= S(52)/S(48) \\S(177) &= S(53)/S(48) \\S(178) &= 1.0-S(173)-S(174)-S(175)-S(176)-S(177) \\S(179) &= 0.0\end{aligned}$$

Predicted Glass in Melter

$D(54) = S(95) - S(92)$
 $D(55) = S(173)*S(95) - S(180)*S(92)$
 $D(56) = S(174)*S(95) - S(181)*S(92)$
 $D(57) = S(175)*S(95) - S(182)*S(92)$
 $D(58) = S(176)*S(95) - S(183)*S(92)$
 $D(59) = S(177)*S(95) - S(184)*S(92)$
 $S(78) = S(54)-S(55)-S(56)-S(57)-S(58)-S(59)$
 $S(79) = 0.0$
 $S(180) = S(55)/S(54)$
 $S(181) = S(56)/S(54)$
 $S(182) = S(57)/S(54)$
 $S(183) = S(58)/S(54)$
 $S(184) = S(59)/S(54)$
 $S(185) = 1.0-S(180)-S(181)-S(182)-S(183)-S(184)$
 $S(186) = 0.0$

Canister

$D(60) = S(92)$
 $D(61) = S(132)*S(92)$
 $D(62) = S(133)*S(92)$
 $D(63) = S(134)*S(92)$
 $D(64) = S(135)*S(92)$
 $D(65) = S(136)*S(92)$
 $S(80) = S(60) - S(61) - S(62) - S(63) - S(64) - S(65)$
 $S(81) = 0.0$
 $S(187) = S(61)/S(60)$
 $S(188) = S(62)/S(60)$
 $S(189) = S(63)/S(60)$
 $S(190) = S(64)/S(60)$
 $S(191) = S(65)/S(60)$
 $S(192) = 1.0-S(187)-S(188)-S(189)-S(190)-S(191)$
 $S(193) = 0.0$

APPENDIX B

DEFINITION OF STATE VARIABLES IN THE MASS BALANCE MODEL

APPENDIX B

DEFINITION OF STATE VARIABLES IN THE MASS BALANCE MODEL

(NOTE: Masses and vessel levels are in units of KG, flow rates are in kg/h)

- S(1) = Total Mass in WLST
- S(2) = Mass Heat Producers in WLST
- S(3) = Mass "Other Waste Constituents" in WLST
- S(4) = Mass Na_2O in WLST
- S(5) = Mass B_2O_3 in WLST
- S(6) = Mass SiO_2 in WLST
- S(7) = Mass "Other Glass Formers" in WLST
- S(8) = Total Mass in WCT
- S(9) = Mass Heat Producers in WCT
- S(10) = Mass "Other Waste Constituents" in WCT
- S(11) = Mass Na_2O in WCT
- S(12) = Mass B_2O_3 in WCT
- S(13) = Mass SiO_2 in WCT
- S(14) = Mass "Other Glass Formers" in WCT
- S(15) = Total Mass in FPT
- S(16) = Mass Heat Producers in FPT
- S(17) = Mass "Other Waste Constituents" in FPT
- S(18) = Mass Na_2O in FPT
- S(19) = Mass B_2O_3 in FPT
- S(20) = Mass SiO_2 in FPT
- S(21) = Mass "Other Glass Formers" in FPT
- S(22) = Total Mass in Melter Feed Tank (MFT)
- S(23) = Mass Heat Producers in MFT
- S(24) = Mass "Other Waste Constituents" in MFT
- S(25) = Mass Na_2O in MFT
- S(26) = Mass B_2O_3 in MFT
- S(27) = Mass SiO_2 in MFT
- S(28) = Mass "Other Glass Formers" in MFT
- S(29) = Total Mass in Cold Cap
- S(30) = Mass Heat Producers in Cold Cap
- S(31) = Mass "Other Waste Constituents" in Cold Cap
- S(32) = Mass Na_2O in Cold Cap
- S(33) = Mass B_2O_3 in Cold Cap
- S(34) = Mass SiO_2 in Cold Cap
- S(35) = Total Mass in Melter Glass
- S(36) = Mass Heat Producers in Melter Glass

S(37) = Mass "Other Waste Constituents" in Melter Glass
 S(38) = Mass Na_2O in Melter Glass
 S(39) = Mass B_2O_3 in Melter Glass
 S(40) = Mass SiO_2 in Melter Glass
 S(41) = Predicted Total Mass in Melter Feed Tank (MFT)
 S(42) = Predicted Mass of Heat Producers in MFT
 S(43) = Predicted Mass of "Other Waste" in MFT
 S(44) = Predicted Mass of Na_2O in MFT
 S(45) = Predicted Mass of B_2O_3 in MFT
 S(46) = Predicted Mass of SiO_2 in MFT
 S(47) = Predicted Mass of Frit in MFT
 S(48) = Predicted Total Mass in Cold Cap
 S(49) = Predicted Mass of Heat Producers in Cold Cap
 S(50) = Predicted Mass of "Other Waste" in Cold Cap
 S(51) = Predicted Mass of Na_2O in Cold Cap
 S(52) = Predicted Mass of B_2O_3 in Cold Cap
 S(53) = Predicted Mass of SiO_2 in Cold Cap
 S(54) = Predicted Total Mass in Melter Glass
 S(55) = Predicted Mass of Heat Producers in Melter Glass
 S(56) = Predicted Mass of "Other Waste" in Melter Glass
 S(57) = Predicted Mass of Na_2O in Melter Glass
 S(58) = Predicted Mass of B_2O_3 in Melter Glass
 S(59) = Predicted Mass of SiO_2 in Melter Glass
 S(60) = Total Mass in Canister
 S(61) = Mass of Heat Producers in Canister
 S(62) = Mass of "Other Waste" in Canister
 S(63) = Mass of Na_2O in Canister
 S(64) = Mass of B_2O_3 in Canister
 S(65) = Mass of SiO_2 in Canister
 S(66) = Sum of Mass of Melted Glass and Cold Cap
 S(67) = Mass of H_2O in WLST
 S(68) = Mass of H_2O in WCT
 S(69) = Mass of H_2O in FPT
 S(70) = Mass of H_2O in Melter Feed Tank
 S(71) = Mass of "Other Glass Formers" in Cold Cap
 S(72) = Mass of H_2O in Cold Cap
 S(73) = Mass of "Other Glass Formers" in Melter Glass
 S(74) = Mass of H_2O in Melter Glass
 S(75) = Predicted Mass of H_2O in Melter Feed Tank
 S(76) = Predicted Mass of "Other Glass Formers" in Cold Cap
 S(77) = Predicted Mass of H_2O in Cold Cap
 S(78) = Predicted Mass of "Other Glass Formers" in Melter Glass
 S(79) = Predicted Mass of H_2O in Melter Glass
 S(80) = Mass of "Other Glass Formers" in Canister
 S(81) = Mass of H_2O in Canister

S(82) = Mass Flow Rate Waste to WLST
 S(83) = Mass Flow Rate from WLST to WCT
 S(84) = Mass Evaporation Rate from WCT
 S(85) = Mass Flow Rate from WCT to FPT
 S(86) = Mass Flow Rate of Addition of Frit 1 to FPT
 S(87) = Mass Flow Rate of Addition of FRIT 2 to FPT
 S(88) = Mass Evaporation Rate from FPT
 S(89) = Mass Flow Rate from FPT to Melter Feed Tank
 S(90) = Mass Flow Rate of Slurry Feed to Melter (Cold Cap)
 S(91) = Mass Flow Rate from Cold Cap to Glass Melt
 S(92) = Mass Flow Rate of Glass Out of Melter
 S(93) = Mass Flow Rate of Exhaust Gas (H_2O) Out of Melter
 S(94) = Predicted Mass Flow Rate from FPT to MFT
 S(95) = Predicted Mass Flow Rate from Cold Cap to Glass Melt
 S(96) = Predicted Mass Flow Rate of Exhaust Gas Out of Melter
 S(97) = Wt Fraction of Heat Producers in WLST
 S(98) = Wt Fraction of "Other Waste Constituents" in WLST
 S(99) = Wt Fraction of Na_2O in WLST
 S(100) = Wt Fraction of B_2O_3 in WLST
 S(101) = Wt Fraction of SiO_2 in WLST
 S(102) = Wt Fraction of "Other Glass Formers" in WLST
 S(103) = Wt Fraction of H_2O in WLST
 S(104) = Wt Fraction of Heat Producers in WCT
 S(105) = Wt Fraction of "Other Waste Constituents" in WCT
 S(106) = Wt Fraction of Na_2O in WCT
 S(107) = Wt Fraction of B_2O_3 in WCT
 S(108) = Wt Fraction of SiO_2 in WCT
 S(109) = Wt Fraction of "Other Glass Formers" in WCT
 S(110) = Wt Fraction of H_2O in WCT
 S(111) = Wt Fraction of Heat Producers in FPT
 S(112) = Wt Fraction of "Other Waste Constituents" in FPT
 S(113) = Wt Fraction of Na_2O in FPT
 S(114) = Wt Fraction of B_2O_3 in FPT
 S(115) = Wt Fraction of SiO_2 in FPT
 S(116) = Wt Fraction of "Other Glass Formers" in FPT
 S(117) = Wt Fraction of H_2O in FPT
 S(118) = Wt Fraction of Heat Producers in Melter Feed Tank (MFT)
 S(119) = Wt Fraction of "Other Waste Constituents" in MFT
 S(120) = Wt Fraction of Na_2O in MFT
 S(121) = Wt Fraction of B_2O_3 in MFT
 S(122) = Wt Fraction of SiO_2 in MFT
 S(123) = Wt Fraction of "Other Glass Formers" in MFT
 S(124) = Wt Fraction of H_2O in MFT
 S(125) = Wt Fraction of Heat Producers in Cold Cap
 S(126) = Wt Fraction of "Other Waste Constituents" in Cold Cap

S(127) = Wt Fraction of Na_2O in Cold Cap
 S(128) = Wt Fraction of B_2O_3 in Cold Cap
 S(129) = Wt Fraction of SiO_2 in Cold Cap
 S(130) = Wt Fraction of "Other Glass Formers" in Cold Cap
 S(131) = Wt Fraction of H_2O in Cold Cap
 S(132) = Wt Fraction of Heat Producers in Melter Glass
 S(133) = Wt Fraction of "Other Waste Constituents" in Melter Glass
 S(134) = Wt Fraction of Na_2O in Melter Glass
 S(135) = Wt Fraction of B_2O_3 in Melter Glass
 S(136) = Wt Fraction of SiO_2 in Melter Glass
 S(137) = Wt Fraction of "Other Glass Formers" in Melter Glass
 S(138) = Wt Fraction of H_2O in Melter Glass
 S(139) = Wt Fraction of Heat Producers in Waste
 S(140) = Wt Fraction of "Other Waste Constituents" in Waste
 S(141) = Wt Fraction of H_2O in Waste
 S(142) = Wt Fraction of Na_2O in Frit 1
 S(143) = Wt Fraction of B_2O_3 in Frit 1
 S(144) = Wt Fraction of SiO_2 in Frit 1
 S(145) = Wt Fraction of "Other Glass Formers" in Frit 1
 S(146) = Wt Fraction of H_2O in Frit 1
 S(147) = Wt Fraction of Na_2O in Frit 2
 S(148) = Wt Fraction of B_2O_3 in Frit 2
 S(149) = Wt Fraction of SiO_2 in Frit 2
 S(150) = Wt Fraction of "Other Glass Formers" in Frit 2
 S(151) = Wt Fraction of H_2O in Frit 2
 S(152) = Target Full Level in WCT
 S(153) = Target Concentrated Level in WCT
 S(154) = Target Empty Level in WCT
 S(155) = Target Concentrated Level in FPT
 S(156) = Target Empty Level in FPT
 S(157) = Target Ready Level in Melter Feed Tank
 S(158) = Target Empty Level in Melter Feed Tank
 S(159) = Predicted Wt Fraction Heat Transferred from FPT to MFT
 S(160) = Predicted Wt Fraction Waste Transferred from FPT to MFT
 S(161) = Predicted Wt Fraction Na_2O Transferred from FPT to MFT
 S(162) = Predicted Wt Fraction B_2O_3 Transferred from FPT to MFT
 S(163) = Predicted Wt Fraction SiO_2 Transferred from FPT to MFT
 S(164) = Predicted Wt Fraction Frit Transferred from FPT to MFT
 S(165) = Predicted Wt Fraction H_2O Transferred from FPT to MFT
 S(166) = Predicted Wt Fraction Heat in MFT
 S(167) = Predicted Wt Fraction Waste in MFT
 S(168) = Predicted Wt Fraction Na_2O in MFT
 S(169) = Predicted Wt Fraction B_2O_3 in MFT
 S(170) = Predicted Wt Fraction SiO_2 in MFT
 S(171) = Predicted Wt Fraction Frit in MFT

S(172) = Predicted Wt Fraction H_2O in MFT
 S(173) = Predicted Wt Fraction Heat in Cold Cap
 S(174) = Predicted Wt Fraction Waste in Cold Cap
 S(175) = Predicted Wt Fraction Na_2O in Cold Cap
 S(176) = Predicted Wt Fraction B_2O_3 in Cold Cap
 S(177) = Predicted Wt Fraction SiO_2 in Cold Cap
 S(178) = Predicted Wt Fraction Frit in Cold Cap
 S(179) = Predicted Wt Fraction H_2O in Cold Cap
 S(180) = Predicted Wt Fraction Heat in Melter Glass
 S(181) = Predicted Wt Fraction Waste in Melter Glass
 S(182) = Predicted Wt Fraction Na_2O in Melter Glass
 S(183) = Predicted Wt Fraction B_2O_3 in Melter Glass
 S(184) = Predicted Wt Fraction SiO_2 in Melter Glass
 S(185) = Predicted Wt Fraction Frit in Melter Glass
 S(186) = Predicted Wt Fraction H_2O in Melter Glass
 S(187) = Wt Fraction of Heat Producers in Canister
 S(188) = Wt Fraction of "Other Waste" in Canister
 S(189) = Wt Fraction of Na_2O in Canister
 S(190) = Wt Fraction of B_2O_3 in Canister
 S(191) = Wt Fraction of SiO_2 in Canister
 S(192) = Wt Fraction of Frit in Canister
 S(193) = Wt Fraction of H_2O in Canister
 S(194) = Previous Low Level in Melter Feed Tank + 50.0

APPENDIX C

INITIAL VALUES OF THE STATE VARIABLES IN THE MASS BALANCE MODEL

APPENDIX C

INITIAL VALUES OF THE STATE VARIABLES IN THE MASS BALANCE MODEL

(NOTE: Masses and Levels Are in Units of kg, Flow Rates Are in kg/h)

S(1) = 70000.0	S(42) = 10.834
S(2) = 79.1	S(43) = 372.686
S(3) = 2720.9	S(44) = 89.6
S(4) = 0.0	S(45) = 116.8
S(5) = 0.0	S(46) = 601.6
S(6) = 0.0	S(47) = 89.6
S(7) = 0.0	S(48) = 300.0
S(8) = 2000.0	S(49) = 2.5306
S(9) = 9.728	S(50) = 87.049
S(10) = 334.624	S(51) = 21.03
S(11) = 0.0	S(52) = 27.36
S(12) = 0.0	S(53) = 141.0
S(13) = 0.0	S(54) = 4000.0
S(14) = 0.0	S(55) = 33.742
S(15) = 12467.4	S(56) = 1160.658
S(16) = 33.66	S(57) = 280.4
S(17) = 1156.97	S(58) = 364.8
S(18) = 280.53	S(59) = 1880.0
S(19) = 363.73	S(60) = 0.000001
S(20) = 1879.45	S(61) = 0.0
S(21) = 280.53	S(62) = 0.0
S(22) = 4000.0	S(63) = 0.0
S(23) = 10.834	S(64) = 0.0
S(24) = 372.686	S(65) = 0.0
S(25) = 89.6	S(66) = 4300.0
S(26) = 116.8	S(67) = 67200.0
S(27) = 601.6	S(68) = 1655.648
S(28) = 89.6	S(69) = 8472.53
S(29) = 300.0	S(70) = 2720.0
S(30) = 2.5306	S(71) = 21.03
S(31) = 87.049	S(72) = 0.0
S(32) = 21.03	S(73) = 280.4
S(33) = 27.36	S(74) = 0.0
S(34) = 141.0	S(75) = 2720.0
S(35) = 4000.0	S(76) = 21.03
S(36) = 33.742	S(77) = 0.0
S(37) = 1160.658	S(78) = 280.4
S(38) = 280.4	S(79) = 0.0
S(39) = 364.8	S(80) = 0.0
S(40) = 1880.0	S(81) = 0.0
S(41) = 4000.0	S(82) = 0.0

S(83) = 21000.0	S(134) = 0.0703
S(84) = 0.0	S(135) = 0.0912
S(85) = 0.0	S(136) = 0.47
S(86) = 0.0	S(137) = 0.0703
S(87) = 0.0	S(138) = 0.0
S(88) = 0.0	S(139) = 0.00113
S(89) = 21000.0	S(140) = 0.03887
S(90) = 152.5	S(141) = 0.96
S(91) = 48.8	S(142) = 0.0446
S(92) = 97.6	S(143) = 0.012
S(93) = 103.7	S(144) = 0.2988
S(94) = 21000.0	S(145) = 0.0446
S(95) = 48.8	S(146) = 0.6
S(96) = 103.7	S(147) = 0.0354
S(97) = 0.00113	S(148) = 0.092
S(98) = 0.03887	S(149) = 0.2372
S(99) = 0.0	S(150) = 0.0354
S(100) = 0.0	S(151) = 0.6
S(101) = 0.0	S(152) = 27000.0
S(102) = 0.0	S(153) = 7808.0
S(103) = 0.96	S(154) = 2000.0
S(104) = 0.004864	S(155) = 12467.4
S(105) = 0.167312	S(156) = 2000.0
S(106) = 0.0	S(157) = 5000.0
S(107) = 0.0	S(158) = 2000.0
S(108) = 0.0	S(159) = 0.0027
S(109) = 0.0	S(160) = 0.0928
S(110) = 0.8278	S(161) = 0.0225
S(111) = 0.0027	S(162) = 0.02917
S(112) = 0.0928	S(163) = 0.1507
S(113) = 0.0225	S(164) = 0.0225
S(114) = 0.02917	S(165) = 0.68
S(115) = 0.1507	S(166) = 0.0027
S(116) = 0.0225	S(167) = 0.0928
S(117) = 0.68	S(168) = 0.0225
S(118) = 0.0027	S(169) = 0.02917
S(119) = 0.0928	S(170) = 0.1507
S(120) = 0.0225	S(171) = 0.0225
S(121) = 0.02917	S(172) = 0.68
S(122) = 0.1507	S(173) = 0.008435
S(123) = 0.0225	S(174) = 0.29
S(124) = 0.68	S(175) = 0.0703
S(125) = 0.008435	S(176) = 0.0912
S(126) = 0.29	S(177) = 0.47
S(127) = 0.0703	S(178) = 0.0703
S(128) = 0.0912	S(179) = 0.0
S(129) = 0.47	S(180) = 0.008435
S(130) = 0.0703	S(181) = 0.29
S(131) = 0.0	S(182) = 0.0703
S(132) = 0.008435	S(183) = 0.0912
S(133) = 0.29	S(184) = 0.47

S(185) = 0.0703	S(190) = 0.0
S(186) = 0.0	S(191) = 0.0
S(187) = 0.000001	S(192) = 0.0
S(188) = 0.0	S(193) = 0.0
S(189) = 0.0	S(194) = 2050.0

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