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Process Simulation and Statistical Approaches for Validating Waste Form Qualification Models

**W. L. Kuhn
M. R. Toland
B. A. Pulsipher**

May 1989

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PROCESS SIMULATION AND STATISTICAL APPROACHES
FOR VALIDATING WASTE FORM QUALIFICATION MODELS

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Richland, Washington 99352

ABSTRACT

This report describes recent progress toward one of the principal objectives of the Nuclear Waste Treatment Program (NWTP) at the Pacific Northwest Laboratory (PNL): to establish relationships between vitrification process control and glass product quality. During testing of a vitrification system, it is important to show that departures affecting the product quality can be sufficiently detected through process measurements to prevent an unacceptable canister from being produced. Meeting this goal is a practical definition of a successful sampling, data analysis, and process control strategy.

Simulating a process allows this definition to be tested early in the development of the process, based on whatever hypothetical departures from ideal process behavior can be identified and included in the simulation. Consequently, the NWTP approach to waste form qualification includes:

- simulating the process
- introducing departures from ideal behavior
- analyzing the data as though it were real data in order to determine:
 - the effectiveness of statistical methods to monitor and control the process when departures from ideal behavior occur
 - the impact of detectable departures from ideal behavior on the quality of the product.

A simulation model has been developed and preliminarily tested by applying it to approximate operation of the West Valley Demonstration Project (WVDP) vitrification system at West Valley, New York. Multivariate statistical techniques have been identified and described that can be applied to analyze large sets of process measurements. Information on components, tanks, and time is then combined to create a single statistic through which all of the information can be used at once to determine whether the process has shifted away from a normal condition.

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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 product quality.

An important goal during testing of a vitrification system is to show that departures affecting the product quality can be detected through process measurements without direct product sampling in time to prevent production of an unacceptable canister. That both of these hold is a practical definition of a successful sampling, data analysis, and process control strategy. Process simulation allows this strategy to be tested early in the development of a process, using whatever hypothetical departures from ideal process behavior that can be identified and included in the simulation. Consequently, the NWTP approach to waste form qualification includes:

- simulating the process
- introducing departures from ideal behavior
- analyzing the data as though it were real data in order to determine:
 - the effectiveness of statistical methods to monitor and control the process when departures from ideal behavior occur
 - the impact of detectable departures from ideal behavior on the quality of the product.

Implementation of the approach is not yet complete. However, two important steps have been accomplished and are described in this report. First, a simulation model has been developed and preliminarily tested by applying it to approximate operation of the West Valley Demonstration Project (WVDP) vitrification system at West Valley, New York. A control logic for the WVDP process was approximated and cast in the form of an input file as required by the simulation model. The model includes the capability to simulate random measurement and control errors, systematic errors, and departures from ideal

mixing behavior. This capability generates large sets of simulated process measurements that reflect the existence or absence of systematic errors or departures from ideal behavior. The sets can be investigated using trial data analysis techniques to determine if such errors or departures could be detected during operation of a real process.

Second, multivariate statistical techniques have been identified and described that can be applied to analyze large sets of process measurements. The use of these techniques in process control charting is also described. The techniques collect information on the chemical composition of the materials/slurries and glass at various stages in the vitrification process. This information on components, tanks, and time is then analyzed to create a single statistic through which all of the information can be used at once to determine whether the process has shifted away from a normal condition. Process control charting is then used to examine the statistic and to make decisions about the need for changes in the process.

SIMULATION MODEL

If there were ideal mixing in tanks, then, within the precision and accuracy of measurements, the composition of the feed and glass could be predicted from simple mass balances. A plausible departure from such ideality that could affect the validity of an assumed mass balance model would be sedimentation and resuspension of part of a slurry in tanks. These are addressed in the process simulation. Caking of all of the slurry on the sides of tanks and return of cake to the slurry is also included. Other phenomena can be included as desired.

The simulation of a vitrification process was accomplished by defining:

- Tanks (which might not be process tanks) for which transient mass balances are solved by integrating time derivatives of masses in the tanks
- Phases within tanks that allow water, dissolved solids, undissolved (suspended) solids, and sediment and caked material to be treated separately in the calculations

- Streams connecting tanks
- Events described in terms of volumes of liquid in tanks or of elapsed time, which when detected, interrupt the normal integration over time and cause various actions that modify the process (for example, when streams are turned on or off).

Process control is defined in terms of events, which are either a volume reaching some specified value or time reaching some specified value. Whenever an event occurs, some predetermined control action is taken. Examples of actions are: 1) turning a stream on or off, 2) defining that some condition is true or false (for use in future control decisions), and 3) taking a sample from a tank, etc. Once an event occurs, any number of control actions might follow, including secondary reactions to actions. However, the entire string of actions always begins when an event is detected. The process is simulated as being stochastic by introducing uncertainty into the simulation of certain measurements and actions.

A process control strategy is implemented in a simulation by defining a set of "cases." Each case is described in terms of a set of tests followed by a set of actions. The tests for a case are evaluated using "and" logic--that is, all tests must be satisfied before the case actions are executed. The tests that have been included are for a specified liquid volume occurring in a tank, for a stream flowing or not, and for a flag corresponding to some process condition set true or false.

Currently, seven kinds of actions might be taken, separately or in combination, if a case's tests are met and the case is executed. They are change stream flow, set flag, delay, sample, test contents, add chemicals, and reset tank.

To evaluate the ability of the methods described above to simulate a vitrification process, they were applied to a case patterned roughly after the WVDP system. The simulation is not of this process exactly, because parts of the process and the control strategy are still being determined. Instead, we have included some of the essential features of the process and plausible values for the simulation parameters in order to test the simulation methods.

A strategy for controlling the WVDP vitrification process was constructed that roughly simulates the actual process. We have not attempted to identically simulate the WVDP; instead, we assume the construction is close enough to reality to provide a realistic test of our simulation model. Probably the most significant departure from our understanding of the WVDP strategy is that we have included an additional sampling step.

MULTIVARIATE STATISTICAL TECHNIQUES

The multivariate statistical methods described in the report have been developed in four parts.

1. Models are developed that describe the relationships of the concentrations of chemical components in adjacent tanks as batches progress from tank to tank. The models are formulated in matrix form to facilitate the development and description of a corresponding computational scheme. In the development, the vitrification system is approximated as a feed preparation tank, melter feed tank, and melter; for the WVDP, these would be the CFMUT, melter feed tank, and melter. All tanks are assumed to be perfectly mixed. The effect of any accumulation in the cold cap in the melter is neglected.
2. Multivariate statistical methods are used to develop equations for estimating the true oxide concentrations in tanks. The methods account for correlation between concentrations that would be expected in the data (for example, tank-to-tank and component-to-component). This correlation is particularly important when trying to sense whether the process is statistically stable, or whether it is drifting: whether it has increasing fluctuations or changes in character. One does not need to evaluate how a single variable fluctuates, but how several variables fluctuate together. For example, it may be normal (typical of a stable process) for two measured variables to fluctuate independently of each other, but not for them to fluctuate in unison. Multivariate statistical methods are applied to distinguish between such cases for a large

set of measured variables, or to discover what relationships are normal among complicated combinations of measured variables.

3. Multivariate process control charts are described that can be used for monitoring the oxide concentrations of the frit/waste slurry wherever it is sampled in the process. To control the process based on deviations from normal behavior as discerned from many measurements, taken at several locations and over weeks of time, requires combining all such data into a single statistic. A means of doing this is described that provides a statistic distributed as "Hotelling's T^2 " statistic.
4. The extent of sampling that is required and the assumptions that have been made in the statistical analyses are discussed. This discussion pertains mainly to sampling that is required to build covariance matrices from the process measurements that one wishes to consider when monitoring and controlling the process.

In controlling the process, it is desirable to limit the number of variables whose values are to be constrained. In the case of a waste vitrification system, one important quality characteristic of the glass to be achieved is adequate chemical durability. Such data can be reduced using purely statistical methods. Waste glass "leach" data made available to us were analyzed to examine the relationship between the chemical durability and the composition of the glass. The release of boron into solution after 28 days in a static leach test was taken to be the measure of chemical durability.

The data were analyzed using the "partial least squares" (PLS) method. The dependencies suggest that, to a rough first approximation, the chemical durability depends on the ratio of the weight fractions of sodium and boron to silicon and aluminum.

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Part of the work, that of describing a vitrification process control strategy in terms of "cases" of tests and actions, benefited from close collaboration with similar work funded by the Hanford Waste Vitrification Program, which is conducted by PNL in support of the Hanford Waste Vitrification Plant project. That project is managed by Westinghouse Hanford Company for the U.S. Department of Energy.

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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)^(a). One of the principal objectives of this program is to establish relationships between vitrification process control and glass product quality. Users of the liquid-fed ceramic melter (LFCM) process can use these relationships to establish acceptance of vitrified high-level nuclear waste at licensed federal repositories. These relationships can also minimize examination of radioactive glass without resorting to destructive examination of the canisters.

The NWTP and preceding programs have been developing waste form qualification methods for several years. Current work focuses on defining, developing, and demonstrating an objective and quantitative method for assuring the quality of a canister of vitrified high-level waste (HLW) based on process control and statistical monitoring of process instrumentation. The central objective is to address the quality assurance concerns for glass disposal in a licensed nuclear waste repository with minimal or no sampling of glass from a canister.

1.1 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" 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

(a) Operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

waste form production."^(a) To implement this process, a Waste Acceptance Committee (WAC) has been established. The NWTP at PNL is defined as one of the members of the WAC.

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) The WAC is responsible for coordinating or preparing certain documents called for by the WAP. The principal documents are 1) a Waste Form Description, 2) a Waste Acceptance Preliminary Specification (WAPS), 3) a Waste Form Compliance Plan, 4) a Waste Form Qualification (WFQ) 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 describe how the producer has shown compliance with the specifications.

1.1.1 Implications of the Waste Acceptance Process

The WAP is a challenge to waste form producers in that they must build, in the Office of Civilian Radioactive Waste Management (OCRWM) and the Nuclear Regulatory Commission (NRC) (who will license a repository), confidence that the waste acceptance specifications are being successfully addressed. Waste form producers must understand their process and product as well as or better than the OCRWM, NRC, or associated technical experts if they are to instill confidence that startup of a vitrification facility and glass canister production should proceed. To build this confidence, the Waste Form Qualification Report needs to ensure that

- the uncertainty in the composition and structure (viz., crystallinity) of the glass will be known
- the variability of the product will be acceptable

(a) "Establishment of Waste Acceptance Process and Waste Acceptance Committee," memorandum from W. J. Purcell to distribution, U.S. Department of Energy, Office of Geologic Repositories, July 8, 1985.

- the process and product are well understood such that the process can be controlled to produce an acceptable product.

The first of these assurances is identified from the WAPS as they are proposed for the Defense Waste Processing Facility (DWPF) or the West Valley Demonstration Project (WVDP). The WAPS require the waste form producer to describe the chemical composition of the product and the uncertainty in the composition. We determined the need for the other assurances as follows.

1.1.2 Importance of Demonstrating Process Control

A means has yet to be identified for recycling a canister of glass through a vitrification process. Although some means could be developed in theory, its implementation for canisters of highly radioactive glass would be expensive and probably impractical. Therefore, it seems unlikely this recycling capability will be developed.

Assuming no such capability exists, then, if for some reason a canister is found to be unfit for disposal at a repository, the canister may remain with the waste form producer pending possible remedial action. Alternatively, the repository may accept the canister, assuming some special treatment can be devised such that the repository can be licensed. In the first alternative, the waste form producer will be left with canisters whose future is in doubt. In the second alternative, the repository project will be left with waste forms which leave licensing in doubt.

The difficulty of this choice focuses attention on what must be done before production to ensure that canisters will be acceptable. Even if there is confidence that the means will exist to determine the product quality, there must also be confidence that, once determined, the quality will be considered acceptable.

1.1.3 Importance of Demonstrating Process Understanding

To build confidence that the process and product can be controlled such that the need to recycle a canister is improbable, the waste form producer should demonstrate to OCRWM and NRC that its understanding of the process and product is in accordance with and not contradicted by available data. Such data will consist of the behavior of the process and product as determined by

various means before the start of radioactive operation and the production of canisters of radioactive glass. Specifically, if predicted process and product variability is based on an assumption of ideal mixing in feed tanks and the melter, pilot-scale and nonradioactive full-scale vitrification system data should be shown to support the assumption and not contradict it.

Similarly, if a restrictive relationship between glass composition and resistance to dissolution in water is the basis for controlling product quality through composition, then the relationship should be corroborated by experiments and shown to be consistent with available data.

1.2 PRIOR WORK BY NWTP ON WASTE FORM QUALIFICATION

The basic NWTP approach to waste form qualification was presented by Kuhn and Slate (1983) and has been pursued by the NWTP and its predecessor programs for a number of years (Brouns and Kuhn 1986). The PNL approach includes modeling the process and the product in order to relate process measurements to the composition and cooling history of the glass produced in a canister. The PNL approach specifically addresses the waste form specifications outlined in the WAPS. Reimus et al. (1986) and Kuhn et al. (1986) have described recent advances in using process simulation to demonstrate the role of chemical sampling and analyses and of process models in controlling and estimating the composition of the glass. Pulsipher and Kuhn (1987) have described the use of process control charting as a basis for controlling a vitrification process.

In the work by Reimus et al. (1986), a dynamic simulation of a hypothetical vitrification process was constructed using the SIMAN^(a) simulation software. The equipment and control strategy for the process were described in a set of Fortran statements written as required to supplement the SIMAN simulation framework. This allowed a rapid simulation of one specific, hypothetical process, but alternative equipment or control strategies could not be considered without completely reprogramming the Fortran statements.

(a) SIMAN is a registered trademark of the Systems Modeling Corporation, State College, Pennsylvania.

The result of the simulation was a comparison of a continuously varying, simulated glass composition and a continuously varying, simulated composition as it would be inferred from process measurements. The tank composition inferred from process measurements was equal to the composition most recently determined by sampling the tank. Information about the contents of tanks for prior batches was not utilized.

1.3 NWTP TECHNICAL APPROACH TO WASTE FORM QUALIFICATION MODELING

To develop and demonstrate an understanding of the vitrification process, it is valuable to simulate ideal process operation and plausible departures from ideal operation. The same statistical methods proposed for analyzing actual process data can be used on simulated data. Then, the simulated data can be compared with data from real pilot- or full-scale processes to determine whether the real system behaves as the simulated one. Demonstration that the real and simulated systems behave similarly builds confidence that the processes and events controlling the real system are, in fact, those assumed in simulating the process. Therefore, these processes and events are adequately understood.

An important goal during testing of a vitrification system is to show that departures significant enough to affect the product quality could be detected in time to prevent an unacceptable canister from being produced. It should also be shown that other departures too small to be detected would not significantly decrease the quality of the product. This goal is a practical definition of a successful sampling, data analysis, and process control strategy. Simulation of the process, using any hypothetical departures from ideal process behavior that can be identified, allows a testing of this strategy early in the development of a process.

Application of process simulation to develop and demonstrate an understanding of the vitrification process as identified in the NWTP approach to waste form qualification includes the following steps:

- simulating the process
- introducing departures from ideal behavior

- analyzing the data as though it were real data in order to determine:
 - the effectiveness of statistical methods to monitor and control the process when departures from ideal behavior occur
 - the possible impact of detectable departures from ideal behavior on the quality of the product.

These steps are described further in the following sections.

1.3.1 Process Simulation

The primary software tool is a process simulator that predicts how an ideal vitrification process would behave if its controls were based on uncertain measurements and imprecise actions. The simulator can also describe the overall effect of postulated departures from ideal behavior. The components of the process to be simulated include the transient mass balances over tanks in the vitrification system, the effects of control actions during the course of a vitrification campaign, and the uncertainties in process measurements and control actions. Therefore, the simulation must simultaneously solve differential equations describing the transient mass balances, address discontinuous changes in the equations caused by control actions such as turning streams on or off, and introduce random errors into simulated measurements and control actions.

For example, a melter feed tank would be filled until a volume indicator reached a certain reading. This would be simulated as being the true level plus some random and/or systematic error. Hence, because of measurement error, the tank would be filled to something other than the desired and apparent volume. The simulation must consider intermittent, nonconcurrent flows into and out of tanks (batching operations) and continuous, concurrent flow into and out of a tank, as for the glass in the melter.

1.3.2 Introduction of Departures

In an ideal process, there would be ideal mixing in tanks, and the composition of the feed and glass could be predicted from simple mass balances. A plausible departure from such ideality that could affect the validity of an assumed mass balance model would be sedimentation and

resuspension of part of a slurry in tanks. This departure could, in principle, cause the solids loading in the slurry removed from a tank to be smaller than predicted at one point and then greater than predicted later. Variations would be introduced in the feed or glass composition that would not be predicted based on an ideal model.

Sedimentation and resuspension of solids in a slurry are addressed in the process simulation. Caking of all of the slurry on the sides of tanks and return of cake to the slurry is also included. Other phenomena can be included as needed.

Of course, the actual departures from ideality that will occur are not known; therefore, they cannot be knowingly simulated. However, plausible departures can be postulated, simulated, and the result used to determine what effect they would have on the quality of the product. Sensitivity studies can therefore be done much less expensively than experimental studies on vitrification systems to determine what magnitude of departures the process operator must be able to identify and correct in order to prevent unacceptable shifts in the process.

This process can be continued whenever the ability to know and control the product is challenged on the basis of additional postulated departures from ideality. For any departure that can be simulated, the waste form producer can investigate the potential of the departure to affect product quality without the departure being detected. This does not assure that actual departures from ideality will be addressed, but allows specific concerns to be addressed and evaluated.

1.3.3 Analysis of Simulated Data

To determine the effect of measurement and control errors and departures from ideal behavior on the ability to monitor and control the process, simulated process data must be analyzed as would real process data. This analysis includes inferring compositions from mass balances and controlling the process using process control charting. Before this can be done, effective methods for monitoring and controlling the process must be identified or developed.

The ability to control a vitrification process by applying process control charting to a single measured variable was investigated previously (Pulsipher and Kuhn 1987, Reimus et al. 1986). In this report, we describe the application of multivariate statistical analysis toward monitoring and controlling the process (see Section 7.0). Information is collected on the composition of a number (conceivably, all) of the chemical components in the feed and glass, for batches in each of the tanks (including the melter), and for each repetition of the batching cycle of the vitrification system. This information on components, tanks, and time is then analyzed to create a single statistic through which all of the information can be used at once to determine if the process has shifted away from a normal condition. Process control charting is used to examine the statistic and to make decisions about the need for changes in the process.

1.4 ADVANCES TOWARD IMPLEMENTING THE NWTP APPROACH

Implementation of the approach described above is not yet complete. However, two important steps have been accomplished. First, a simulation model has been developed and tested preliminarily by applying it to approximate operation of the WVDP vitrification system. A control logic for the WVDP process was approximated and cast in the form of an input file as required by the simulation model. The model includes the capability to simulate random measurement and control errors, systematic errors, and departures from ideal mixing behavior. This capability provides for generating large sets of simulated process measurements that reflect the existence or absence of systematic errors or departures from ideality. These process measurements can be investigated using data analysis techniques to determine whether such errors or departures could be detected during operation of a real process.

Second, multivariate statistical techniques have been identified and described that can be applied to analyze large sets of process measurements. Their use in controlling a process through process control charting has also been described.

These advances are discussed in the remainder of the report.

2.0 USE OF SIMAN SIMULATION SOFTWARE

To simulate a vitrification process sufficiently to address waste form qualification issues, it is necessary to provide three basic functions:

- integrate differential equations describing transient mass balances
- detect discrete events, interrupt the integration, and change the differential equations as appropriate before continuing the integration
- simulate uncertainty and errors in measurements and control actions.

One existing simulation tool that fulfills these needs is the commercial software package SIMAN. SIMAN was used by Reimus et al. (1986) in developing their simulation approach and was also used to construct the process simulation model described here. SIMAN is best suited for simulating discrete systems where objects are identified and subjected to various events while proceeding through a queue, such as simulating the flow and assembly of parts through a machine shop. However, it can also simulate continuous systems. It is this dual capability to simulate simultaneously discrete (characterized by events) and continuous (characterized by processes) systems that has made it useful for our purposes. We have circumvented some of the structure of the SIMAN software in order to make its use in simulating a vitrification process much more flexible, especially when considering "what if" scenarios or proposed changes in process design or control.

2.1 STRUCTURE OF SIMAN

As we use it, SIMAN is essentially an algorithm that:

- integrates coupled ordinary differential equations
- repeatedly checks the results of the integration for an "event," defined as time or the value of a variable being integrated reaching a specified value
- calls for specified actions when an event occurs.

The variables being integrated are termed "state" variables. SIMAN uses a Runge-Kutta-Fehlberg fourth-fifth order integration routine. The time step is adjusted to maintain specified accuracies in the state variables, to bring the simulated time during a step to that for which an event has been scheduled, or to bring a state variable during the time step to a value at which an event is to occur. The state variables are described within SIMAN as a one dimensional array "S." The time derivatives of the state variables are described as a corresponding one dimensional array "D." SIMAN uses subroutines written by the user to repeatedly update the D-array, uses the D-array in its time integration routine, and returns an updated S-array to the user-written subroutines that recalculate the S-array. Thus, the process is simulated as described by the state variables and the user-written subroutines describing their time derivatives.

SIMAN calls subroutines named PRIME, STATE, EVENT, and WRAPUP programmed by the user to effect the simulation. PRIME is called by SIMAN at the start of a simulation and, in our case, is the subroutine used to read our input files. The STATE subroutine is programmed to calculate time derivatives of state variables, as discussed above. The EVENT subroutine is programmed to determine what action is to be taken in response to a state event or time event, including the action of periodically reporting the results of the simulation to output files. The subroutine WRAPUP is called by SIMAN at the conclusion of a simulation; it is the least important, being used only to close the input and output files.

2.2 CIRCUMVENTING THE STRUCTURE OF SIMAN

A software interface for SIMAN was written that reads input files describing the process to be simulated and translates the information into a form that can be recognized by SIMAN. The structure of SIMAN itself is thereby circumvented, in that the input files for the simulation make no reference to any of the arrays or subroutines used by SIMAN. Therefore, the user of the process simulation need not understand or refer to the SIMAN software. There need be no reference to the S- or D- arrays in SIMAN, which means the numbering of elements (individual state variables) within these arrays need not be addressed in describing the process to be simulated. This

facility is important, because any attempt to modify or extend the description of a process would likely involve renumbering references to the S- and D- arrays, thereby making such changes both tedious and prone to error.

2.3 INPUT FILES

A number of input files are required by the software interface. The information included in the files is discussed in detail below. The files and their contents are as follows.

- Process File: This is a list of the names of process streams and the names of the tanks where the streams begin and end.
- Component File: This is a list of names of chemical components to be considered in mass balance calculations. For each component, the list includes the target weight fraction in the glass, the fraction of the component that will remain in the glass in the melter (a measure of its volatility), and the relative standard deviation for its measurement during chemical analyses.
- Stream File: This is a list of information including, by stream name, the stream flow rates (when flowing) and a set of parameters describing the access by the stream to different phases in its inlet tank.
- Tank File: This is a list of information about the tanks, listed by tank name, and includes the densities of different phases in each tank and parameters describing the error in measuring the volume in the tank.
- Phase Distribution Default File: This is a list of parameters that describe how each chemical component, listed by component name, will distribute among three phases in a tank. The values are taken to be default values for all tanks. Departures from default values are described separately in the "phase distribution specific file."
- Phase Distribution Specific File: This is a list of the same parameters included in the "phase distribution default file,"

except they are specific to particular tanks, listed by tank name and, for those tanks listed, supersede the default values of the parameters. For example, the parameters for the melter must describe entirely different behavior of chemical components than is typical in a tank full of feed slurry.

- Chemical Addition File: This is a listing of information used to simulate adding chemical components to a tank to create a batch of melter feed that will result in glass of a specific composition. The file includes the maximum solids loading to be allowed when transferring a slurry to a tank and the names of the chemical components to be adjusted toward target values during the chemical addition action.
- Test Contents File: This is a listing of information used to simulate the testing of the contents of a tank to determine whether the contents are acceptable and should be sent on through the process. The file includes the names of the chemical components whose weight fractions, as they would occur in a glass made from the batch, are to be compared to target weight fractions.
- Process Start File: This file lists information about the starting conditions for the process, including initial masses of components in specific tanks, the names of streams that are to be considered flowing at the start of the simulation, and a list of "flags" (which signify the status of certain process situations, as described below) that are to be initially set to "true."
- Case File: This is a file describing the process control strategy in terms of a set of "cases." Each case consists of a set of tests to be passed (for example, whether a stream is on or off, whether liquid in a tank has increased or decreased to a certain volume, etc.) and a set of actions to be taken if all tests are passed (for example, turn a stream on or off, sample the contents of a tank, etc.).

3.0 MASS BALANCE SIMULATION

The simulation of a vitrification process is accomplished by defining the following components, which will be described in further detail below.

- tanks (which might not be process tanks) for which transient mass balances are solved by integration of time derivatives of masses in the tanks
- phases within tanks that allow water, dissolved solids, undissolved (suspended) solids, and sediment and caked material to be treated separately in the calculations
- streams connecting tanks to each other
- events described in terms of volumes of liquid in tanks or of elapsed time which, when detected, interrupt the normal integration over time and cause various actions to occur that modify the process (for example, turning streams on or off).

3.1 DEFINITION OF TANKS

In the "tanks" input file, each tank in the process is described in terms of the distribution of each incoming chemical component among three phases and the density of each of the phases in the tank. The streams that enter or leave the tank are defined in the "process" input file. The tanks have no prescribed volume; the volume is manifest only in those control actions that specify the volumes at which liquid transfers begin or end.

3.2 DEFINITION OF PHASES

Five phases are defined to exist in each tank to simulate the disposition of chemical species upon entering tanks, leaving tanks, and while in tanks. They are 1) water, 2) dissolved solids, 3) suspended undissolved solids, 4) undissolved solids settled on the bottom of a tank, and 5) dissolved and undissolved solids caked on the sides of a tank above the liquid level. Phase 1 is distinct from phase 2 to allow an evaporation process to be described. Phases 3 and 4 allow settling and resuspension of solids to be

addressed and allow separation of solids during slurry sampling to be addressed. Phase 5 allows caking and redissolution of cake to be addressed.

3.3 DEFINITION OF STREAMS

Each stream in the process is described in the "process" input file by its inlet and outlet tanks and in the "stream" input file by its flow rate. The simulation continuously determines whether each stream is flowing at any given time. In the "stream" input file, the distribution of mass from a tank into a stream is described in terms of the fraction of the volumes of each of Phases 1 through 3 in the tank that contribute to the volumetric flow rate of the stream. For example, a stream's volumetric flow rate could consist of contributions from Phases 1, 2, and 3 in the ratio 1.0:0.01:0.01, which might represent evaporation from phase 1 (water) with 1% entrainment from Phases 2 and 3. This ratio is stored in an array VOLSEP defined for this purpose and used to calculate mass flows in streams and transient mass balances in tanks. This is discussed further in Section 5.2.

3.4 DEFINITION OF EVENTS

Process control is defined in terms of events that are to be detected by SIMAN. These can be either a "state event," defined as a state variable passing a specified value in a specified direction, or a "time event," defined as the simulated time reaching a specified value. Whenever an event occurs, some predetermined control action is taken. Examples of actions include turning a stream on or off, defining that some condition such as completion of a sample analysis is true or false (for use in future control decisions), and taking a sample from a tank. Once an event occurs, any number of control actions might occur, including secondary reactions to actions. However, the entire string of actions always begins when an event is detected and SIMAN interrupts its integration over time.

3.5 SIMULATING DETECTION OF AND RESPONSE TO LIQUID VOLUMES

The volumes of tanks are continuously recomputed during a simulation from the masses of the phases in the tanks and the phase densities. A

portion of SIMAN's S-array is reserved for use in describing state events. SIMAN detects state events in terms of a state variable passing a prescribed limit in a prescribed direction, as noted above. Therefore, to detect tank volumes passing specified limits, reserved elements of the S-array need to be calculated as the difference between the volume of a specific tank and the prescribed limit. This difference is multiplied by minus one if the event to be detected is passing the limit in the negative (volume decreasing) direction. When the event occurs, the corresponding state variable (element of the S-array) will pass zero in the positive direction, regardless of the actual specified limit or direction for the corresponding tank volume.

The data describing such "volume events" are provided to the simulation in an input file that defines process control actions. The events are listed by event name, tank name, limit, and direction. Each event is given a number by the subroutine reading the input file, and this number is then specified as the number of the state variable whose value will be calculated as described above to indicate when a volume event has occurred.

Whenever one of these state variables passes zero in the positive direction, SIMAN stops the integration, calls the EVENT subroutine, and passes along the number of the state event that has been detected. We construct the "experiment" file describing state events to the SIMAN software such that the numbers of the events are the same as the numbers of the state variables being checked. These are in turn the numbers assigned to the various volume events described in the input file defining process control actions. Hence, when an event is detected, SIMAN returns the number of the volume event that has been detected, and then, based on this number, the appropriate action can be identified and taken.

The significance of this approach is that the "experiment" file is the same regardless of the description of the volume events. The file is always a list of state events where the number of the state variable being checked is the same as the number of the state event, and the event always consists of the state variable passing zero in the positive direction. Therefore, the "experiment" file does not need to be understood or accessed by the user; all changes to the process or the control strategy are described instead in input

files where state variable numbers or event numbers are unknown by the user. This allows the process to be described in terms familiar to the user (names of equipment and control actions, masses and volumes, times and flow rates, etc.) and independent of any knowledge or understanding of SIMAN itself.

3.6 SIMULATING DELAYS

SIMAN includes subroutines that can be called to schedule events to occur after a prescribed elapsed time, where the event is identified in the Fortran call statement by a number. To circumvent the need to identify events by separate Fortran statements, we invoked a generic "delay" event that can be described in an input file, and whose effect is to cause a "flag" (a true/false indicator of some named condition) to be set false during the delay and true before or after the delay. When a scheduled event occurs and the EVENT subroutine is called, a single event number is passed back from SIMAN which indicates that the event is the end of a delay. At the same time, SIMAN passes back an "entity" number, which is essentially a sequence number for events. When a delay is scheduled, the entity number is saved and associated with the name, delay time, and name of the flag to be set for the particular delay. When the event detected by SIMAN is a delay, the value of the entity number that was assigned by SIMAN to the event is used to identify which delay has been completed and then to select the correct flag to be set as the result.

3.7 INTRODUCTION OF UNCERTAINTIES

The process is simulated as being stochastic by introducing uncertainty to specific measurements and actions in the following manner.

- The act of sampling a slurry is treated as though collecting suspended solids from the liquid is a random process characterized by a normal distribution centered on equal access to liquid and suspended solids by the sampler with a specified standard deviation (this is discussed further in Section 4.2.4).
- The chemical analysis of samples is treated as though the reported individual weight fractions are random, not correlated, and

described by a normal distribution centered on the true weight fractions with a specified relative standard deviation.

- The detection of events by comparing volumes in tanks with specified values is treated as though the measurement of the volume is random and described by a normal distribution centered on the actual volume with a specified relative standard deviation.
- The addition of chemical components is treated as random and described by a normal distribution centered on the calculated masses to be added and with a specified relative standard deviation.

4.0 DESCRIPTION OF PROCESS CONTROL STRATEGY IN TERMS OF "CASES"

In a simulation, the control logic for a vitrification process is described in input files as a set of "cases." For example, one case may be that the tank supplying the waste to be vitrified has been emptied. At that point, the stream transferring waste from the tank to an evaporation tank would be turned off. Other actions, such as setting flags true or false, might also then occur; for example, a flag named "waste available" might be set to false, thus affecting whether some other actions can be taken later.

Each case consists of at least one test and one action. In the example above, the test would be that the volume of liquid in the tank has descended to a certain level, and the actions would be to turn off the stream and to set the flag to false.

In principle, there can be any number of tests and actions per case, although the simulation model limits the number to 10 at present. All of the tests must be satisfied before any action described in the case is taken. When all tests are satisfied, all actions for the case are taken. When all the tests for a case are satisfied and the associated actions are taken, the simulation model checks to see whether the actions taken cause any tests for other cases to be satisfied. If so, the model checks these cases to see if their tests are satisfied. If they are, the associated actions for that case are taken, and then the process repeats until actions taken result in no additional cases' tests being satisfied. At that point, control of the simulation reverts to SIMAN, and the integration over time resumes and continues until stopped by a state event or scheduled event.

Each case is described in a "case" file in terms of a set of tests ending with the entry "END TESTS," followed by a set of actions ending with the entry "END ACTIONS." The case begins with an entry providing the name of the case and ends with the "END ACTIONS" entry. Sections 4.1 and 4.2 describe the kinds of tests and actions that can be simulated using our model.

4.1 TESTS

The tests for a case are evaluated using "and" logic. That is, all tests must be satisfied before the case actions are executed. Therefore, the order in which they appear in the case file is irrelevant. Each test is described by a set of contiguous entries in the case file and begins with one of the test type designators VOLUME, STREAM, or CONDITION, as discussed below.

4.1.1 Volume

The volumes of tanks can be tested to determine whether a given liquid level, expressed in terms of the liquid volume, has been reached in either the upward or downward direction. This test is described in the case file by a sequence of five entries:

- the designator "VOLUME"
- an arbitrary descriptive name for the test
- the name of the tank whose volume is to be checked
- a "T" or "F" designating whether it is true or false that the check is for an increasing volume (that is, "F" signifies that a decreasing volume is to be checked)
- the value the volume is to be checked against.

For example, the set of entries

```
VOLUME
MELTER FEED TANK HIGH ENOUGH
MELTER FEED TANK
T
5000
```

would cause the volume of a "melter feed tank" crossing the value 5000 in the upward direction to be a necessary condition for the case in which this test appears to be executed. The name "melter feed tank high enough" is arbitrary and is included as an aid to understanding the case file. The tank name

"melter feed tank" would have to match exactly the name of the tank given in the input file listing the names of process streams and the names of tanks at their inlets and outlets.

4.1.2 Stream

Streams can be tested to determine whether or not they are flowing. This is described in the case file by a set of three entries: the designator "STREAM," the name of the stream to be tested, and a "T" or "F" signifying that the test is for the stream to be flowing or not flowing, respectively. For example, the set of entries

```
STREAM
MFT TO MELTER
F
```

would include as a necessary condition for the case that the stream named "MFT to melter" be flowing. This test could be included to cause the case to not be executed unless necessary--that is, unless the stream is not already flowing.

4.1.3 Flags

The most flexible test is that of a named condition, termed a "flag." A flag is a true/false indicator of the status of the condition. This is described in the case file by a set of three entries: the designator "CONDITION," the name of the flag (that is, the name of the condition represented by the flag), and a "T" or "F" signifying that the test is for the flag to be set true or false, respectively. For example, the set of entries

```
CONDITION
MELTER FEED SAMPLED
T
```

would include as a necessary condition for the case that the condition "melter feed sampled" be true, which could signify that the contents of a melter feed tank have been sampled. This test could be included so that the feed is not sent to the melter until it has been sampled.

4.2 ACTIONS

There are currently seven kinds of actions that might be taken, separately or in combination, if a case's tests are met and the case is executed. Up to ten actions can be included in a single case, although this number can be increased if necessary. The actions included in a case are executed in the order in which they appear in the case in the case file. Each action is described by a set of contiguous entries in the case file, and begins with one of the action type designators: STREAM, SET FLAG, DELAY, SAMPLE, TEST CONTENTS, CHEMADD, and RESET TANK, as discussed below.

4.2.1 Streams

One of the more obvious actions that must be described is that of turning a stream on or off. This action is described in the case file by a set of four entries: the action type designator "STREAM," a name assigned to the action, the name of the stream, and a "T" or "F" signifying that the stream is to be turned on or off, respectively. For example, the set of entries

```
STREAM
TURN ON MELTER FEED
MFT TO MELTER
T
```

would cause the stream "MFT to melter" to be turned on when the case in which this action appears is executed. The action name "turn on melter feed" is arbitrary and is included as an aid to understanding the case file.

4.2.2 Flags

Another obvious action that must be described is that of setting a flag to true or false. This action is described in the case file by a set of three entries: the action type designator "SET FLAG," the name of the flag, and a "T" or "F" signifying that the flag is to be set true or false. For example, the set of entries

```
SET FLAG
MFT FILL CYCLE COMPLETE
T
```

would cause a flag named "MFT fill cycle complete" to be set true when the case in which this action appears is executed.

4.2.3 Delays

Actions can be executed at a specified period of time after a case is executed by invoking a delay action. This action is described in the case file by a set of four entries: the action type designator "DELAY," a name assigned to the action, the name of a flag to represent whether the delay is in progress or not, and the delay time. The name of the action is arbitrary and is included as an aid to the programmer in writing, editing, and understanding the case file.

The effect of the delay action must be through a complementary "condition" test in some other case. When the delay action occurs, the simulation sets the associated flag to "false" (F) (signifying delay not completed), and calls a SIMAN subroutine that schedules an event to occur after the specified delay time. When this event occurs, it is detected by the simulation as a "delay" event, the appropriate delay is identified, and the associated flag is identified and set to "true" (T) (signifying delay completed). When this happens, any case that includes this flag in a "condition" test will be checked to see whether all of its tests are satisfied. If the "condition" test is the only test, completion of the delay is both necessary and sufficient for execution of this case. Thus, the case will be executed as soon as the delay is complete. If the case includes other tests, completion of the delay will be a necessary but not sufficient condition, and the case may not be executed immediately.

4.2.4 Sampling

The process of sampling the contents of tanks is central to waste form qualification. This action is described in the case file by a set of six entries:

- the action type designator "SAMPLE"
- an arbitrary descriptive name assigned to the action
- the name of the tank to be sampled

- the number of samples to be removed from the tank
- the number of chemical analyses to be done on each of these samples
- the standard deviation of the weight given to access by the sampler to the suspended solids phase in the liquid in the tank. For example, the entries

SAMPLE

SAMPLE WASTE IN CFMUT

CFMUT

3

3

0.02

would cause sampling of the "CFMUT" tank to be simulated, where three samples are taken and each is subjected to chemical analysis three times, and where the weight given to access to the suspended solids phase during the sampling is randomly varied with a standard deviation of 0.02.

The simulated sampling process is described below.

1. A liquid sample is drawn as though into a process stream. Any separation of suspended solids from the remainder of the liquid is assumed to be describable in terms of the model for an ordinary process stream inlet. "Separation at Stream Inlet" under "Equations for Mass Balance" (Section 5.0) discusses this concept further.
2. The mass and volume of the sample are measured with no error (error could be introduced into the simulation if desired). The density is calculated, averaged over the separately drawn samples, and reported as total mass per unit volume of liquid.
3. The samples are each vitrified in a laboratory and the mass of the remaining nonvolatiles in the samples are reported. The resulting glasses are subjected to chemical analysis. The density of nonvolatiles is calculated, averaged over separately drawn samples, and reported as oxide mass per unit volume of liquid.

4. For each sample drawn, one or more chemical analyses are performed for each nonvolatile chemical component. A random measurement error described by a relative standard deviation is assumed to perturb each measurement. The result for each measurement is averaged over all analyses for all samples, and is stored as the average weight fraction of nonvolatile chemical components in glass made from the sample.

The results are stored under the name of the sample action, rather than the name of the tank; the tank could have more than one sample taken per batch during the simulation. The name of the sample action is arbitrary.

4.2.5 Evaporation

Because the waste to be vitrified is typically too dilute to be used in making a feed that results in glass with the desired waste loading, it must first be evaporated. Evaporation is treated as a separate action. It is described in the case file by a set of seven entries:

- the action type descriptor "EVAPORATE"
- an arbitrary descriptive name assigned to the action
- the name of the sample action whose results are to be the basis for the evaporation action (identified in the simulation as "EVAPSAMPLE")
- the name of the process stream to be turned on to effect the evaporation (the stream must be defined such that it accesses (removes) only Phase 1 (water) in order to simulate evaporation)
- the name of the volume test by which the liquid volume at the start of the evaporation is to be determined (identified in the simulation as the "FILLVOLCHECK")
- the name of the volume test to be used in a case that will stop the evaporation (identified in the simulation as the "EVAPVOLCHECK")
- the solids loading desired at the end of the evaporation. For example, the entries

EVAPORATE

EVAPORATE CFMUT

SAMPLE WASTE IN CFMUT
CFMUT EVAPORATION
CFMUT AT FILL LEVEL
CFMUT AT CONCENTRATION LEVEL
0.71

would cause the contents of the "CFMUT" tank to be evaporated to a weight fraction of water of 0.71 by turning on the stream "CFMUT evaporation" and then turning it off when the volume decreased to a calculated value detected by the volume test named "CFMUT at concentration level," and where this volume is calculated from the weight fraction of water, the initial contents of the tank described by the results of the sample action named "sample waste in CFMUT," and the initial volume in the tank, assumed to be that detected by the volume test named "CFMUT at fill level" that caused the case including the "evaporate" action to be executed.

The evaporation action is implemented as follows.

1. The volume in the tank at the start of the evaporation action is defined to be the volume at which the test "FILLVOLCHECK" interrupted the simulation and caused the evaporation action to begin.
2. The results of "EVAPSAMPLE" are used to determine the solids loading in the tank before evaporation.
3. The amount of water to be removed to concentrate the contents of the tank to the desired final weight fraction of water (specified as the last entry in the case file) is calculated, and from this, the desired final volume in the tank is calculated.
4. A separate case must be created that will stop the evaporation. The case must include a volume test with the same name as given to the variable "EVAPVOLCHECK." The volume specified for that volume check is computed in advance during the evaporation action and passed to it by inserting the value in an array in memory. This causes the evaporation, which is only begun during the evaporate action, to be ended by a different case at the correct volume. This approach is necessary since the correct volume cannot be known in advance and specified in the case

file. The volume specified in the case file is never used and is superseded by a value inserted into the array as described above.

5. The process stream is turned on to begin the evaporation.

Therefore, the "evaporate" action calculates the volume in the tank where evaporation is to stop and starts the evaporation by turning on the appropriate process stream. SIMAN then resumes control until interrupted by a volume test that will turn off the stream when the volume of liquid in the tank decreases to the value calculated by the "evaporate" action.

4.2.6 Addition of Chemical Components

The addition of chemical components to a tank must be simulated; it is the principal action by which the composition of the glass is controlled. Basing the approach used here on the operating strategy for the WVDP, we assume there are a number of chemical components whose weight fraction in the glass is to be adjusted to a target value. The addition of chemicals is described in the case file by a set of seven entries:

- the action type designator "CHEMADD"
- an arbitrary descriptive name assigned to the action
- the name of the tank to which chemical components are to be added
- the name of the sample action to be used as the basis for computing the addition of chemical components
- the maximum volume in the tank to be allowed after addition of chemical components
- the weight fraction of water in the tank to be achieved as a result of the addition
- the name of a flag.

For example, the entries

CHEMADD

CFMUT CHEMADD

CFMUT

SAMPLE WASTE IN CFMUT

5500.

0.65

CFMUT VOL ADJUST NEEDED

would cause chemicals to be added to the "CFMUT" tank according to calculations based on the result of the sample action named "sample waste in CFMUT." Water would be added with the chemicals to achieve a final water weight fraction in the resulting slurry of 0.65. If this would cause the resulting volume of the slurry to exceed 5500 gallons, then the addition step is not executed, and instead a flag named "CFMUT vol adjust needed" is set to true.

In the simulation, the action proceeds as follows for the tank to which chemical components are to be added. The average weight fraction among nonvolatile species for the liquid in the tank is known from a sample action, as is the mass of nonvolatiles (that is, oxides remaining after vitrification) per unit volume of liquid sample. Assuming that these values are true for the tank as a whole, then we have

$$x_{it}M_g = x_{iw}M_w + M_{ia} = x_{iw}\rho_w V_w + M_{ia} \quad (4.1)$$

where x = weight fraction among oxides

M = mass of oxide

ρ = density, mass per unit of volume of sample

i = chemical component i

t = "target value"

g = "in the glass"

w = "in the waste in the tank"

a = "to be added."

Equation (4.1) is to be satisfied for a set of components specified in the "chemadd" input file. For one of the components, no mass needs to be added to that already present in the waste in the tank to achieve the target glass composition. This component is designated the "pivot oxide," denoted by the symbol "p." For the pivot oxide we have

$$x_{pt}M_g = x_{pw}\rho_w V_w, \text{ or } M_g = \frac{x_{pw}}{x_{pt}} \rho_w V_w \quad (4.2)$$

Substituting for M_g in Equation (4.1) gives

$$M_{ia} = x_{it} \left[\frac{x_{pw}}{x_{pt}} - x_{iw} \right] M_w \quad (4.3)$$

Since the mass added must be positive, we must have

$$\frac{x_{pw}}{x_{pt}} > \frac{x_{iw}}{x_{it}} \quad \text{for all } i \neq p \quad (4.4)$$

This condition must be satisfied by the pivot oxide. Thus, the pivot oxide is found to be the oxide (component) for which the left side of Equation (4.4) is largest. Once the pivot oxide is determined, the mass of glass that would result from the batch of feed is calculated from Equation (4.2). Subsequently, the masses of chemical components to add to the tank to make up the batch are calculated from Equation (4.3).

We assume that the chemical components are added in the form of a slurry, and that the amount of water added by the slurry should achieve the desired water weight fraction in the slurry. If the resulting volume of slurry in the tank is greater than the specified maximum volume, the chemical addition step is not executed. Instead, a flag is set to signify that some of the waste must be drained from the tank before a chemical addition step can be attempted. The flag allows cases to test whether an addition of chemical components has occurred. A set of cases needs to be defined that will cause the tank to be partially drained and then will call the CHEMADD action for the tank again.

4.2.7 Testing Sample Results

Because the addition of chemical components to form a feed to the melter will be imprecise and be computed based on imprecise process measurements,

the resulting liquid may need to be sampled and then accepted or rejected based on the sample. The test of interest is a comparison of the target glass composition to the apparent composition of the glass that would result from vitrifying the sample. To address this, a "test contents" action has been provided. This action is described by five entries in the case file: the action type descriptor "TEST CONTENTS," an arbitrary descriptive name assigned to the action, the name of the sample action whose results are to be tested, the name of a flag to be set to signify if the contents are acceptable or not, and a tolerance for the test. For example, the entries

```
TEST CONTENTS
TEST MFT CONTENTS
SAMPLE MFT
MFT CONTENTS ACCEPTABLE
0.0625
```

would cause the apparent composition of glass that would be made from the feed, based on the results of the sample named "sample MFT," to be tested against the target glass composition, defined in the "components" input file, with a tolerance of 0.0625. If the result is acceptable, a flag named "MFT contents acceptable" is set to "true"; otherwise, it is set to "false."

The test and its tolerance are defined as follows. A set of components to be tested is defined in the "test contents" input file. The differences between weight fractions for each component reported from the sample action and their target weight fractions are divided by the target weight fractions. The result for each component is squared, and the squares are summed. The resulting sum is checked to see if it is less than or equal to the tolerance. If so, the result is defined as acceptable. Therefore, the value of the tolerance is a bound on the largest square of the relative deviation between a component's weight fraction in the glass that would be made from the sampled liquid and the target composition. In this example, the largest relative deviation in weight fraction could be the square root of 0.0625, or 0.25 (25%). That is, if the target weight fraction for some component were 0.20, it would be allowed to vary at most from 0.15 to 0.25. Any desired tolerance can be imposed.

4.2.8 Resetting Tank Masses

The canister is treated in the simulation as a tank. When the canister is replaced after it is full, the replacement must be simulated by resetting the masses of all components in the tank to zero. The simulation is described in the case file by a set of three entries: the action type descriptor "RESET TANK," an arbitrary descriptive name assigned to the action, and the name of the tank to be reset. For example, the entries

```
RESET TANK  
NEW CANISTER IS EMPTY  
CANISTER
```

would cause the tank whose name is "canister" to have the masses of all components in the tank set to zero.

4.2.9 Batch Report

The basic output from the simulation is a report of the volume of liquid in a tank and the composition of the glass that would be made from it. This is described as an action in the case file by four entries:

- the action type designator "BATCH REPORT"
- an arbitrary descriptive name assigned to the action
- the name of the sample upon which the report is based
- a "T" or "F" signifying that the report is for the beginning of a batch or for the end, respectively.

Each time the action is called with a "T" signifying that it is the start of a batch, a batch number for the tank to which the sample name pertains is incremented by one. This indicates which batch in a sequence of batches for a given task is being reported. For example, the entries

```
BATCH REPORT  
REPORT MFT BATCH  
SAMPLE MFT  
T
```

would cause the apparent volume (that is, the actual volume plus measurement error) to be reported as the starting volume for a new (incremented) batch number. The weight fractions of components in the glass that would result from the liquid sample are reported. Standard deviations of the weight fractions are reported as well. (Standard deviations are calculated as part of the sample action, if the total number of chemical analyses is greater than one.)

5.0 EQUATIONS FOR MASS BALANCE

The basic equation for the transient balances of mass in the process is

$$\frac{dM(\theta, i, \phi)}{dt} = \frac{dM(\theta, i, \phi)}{dt} \Big|_{in} - \frac{dM(\theta, i, \phi)}{dt} \Big|_{out} + \frac{dM(\theta, i, \phi)}{dt} \Big|_{departures} \quad (5.1)$$

where M is the mass in tank θ of component i in phase ϕ , t is time, and "departures" denotes changes to the mass caused by departures from ideal process behavior. The departures currently addressed are sedimentation and caking, as discussed below. The values of θ and i are the numbers of the tanks and components established by the simulation code from the "process" and "component" input files. These time derivatives of mass are calculated in the "STATE" subroutine and passed to SIMAN as values in the D-array of time derivatives of state variables. After each time integration step, new values of M are obtained from SIMAN through the S-array of state variables.

To simulate the separation of mass as streams enter or exit the tanks, the code addresses disposition of chemical components to the phases in a tank upon entering the tank and the accessibility of the phases in a tank to a stream exiting the tank. These are discussed below.

5.1 SEPARATION AT STREAM OUTLET

We assume that, for a given tank, each chemical component always distributes among the water, dissolved solids, and undissolved solids phases in the same ratio. This ratio for a given tank, component, and phase is described in the simulation code by a three-dimensional array PHASEDISTR, represented below as $\Omega(\text{tank}, \text{comp}, \text{phase})$. The array PHASEDISTR is defined in two input files: "phase distribution default" and "phase distribution specific." The "default" file describes a default array for components and phases for all tanks, and the "specific" array corrects the array for those tanks for which the default array is incorrect. A default file is defined because most tanks contain a slurry whose components can be assumed to distribute approximately the same way, and hence would have the same PHASEDISTR array. Departures from the default array can be used to describe

special behavior. For example, for the WVDP, the mass flowing into the cold cap will ultimately become either part of the glass, part of the contents of a submerged bed scrubber in the off-gas stream, or part of the off gas itself. This distribution is modeled by considering Phases 1, 2, and 3 of a cold cap "tank" to flow into separate streams and then to the three destinations. The PHASEDISTR array for this "tank" can be assigned values such that the components distribute to the phases the way they are to distribute to the destinations. It then remains to define three streams that each access only one of the phases.

The rate of increase of mass of a component in a phase in a tank is given by

$$\left. \frac{dM(\Theta, i, \phi)}{dt} \right|_{in} = \Omega(\Theta, i, \phi) \sum_s^{in} \rho(s, i) F(s) \quad (5.2)$$

where the summation is over all streams s flowing into the tank Θ , Ω is defined above, $\rho(s, i)$ is the mass concentration of component i in stream s , and $F(s)$ is the volumetric flow rate of stream s .

5.2 SEPARATION AT STREAM INLET

Each stream can access Phases 1 through 3 in a tank. The access to phase ϕ by stream s is described in the simulation by the array VOLSEP $\psi(\phi, s)$, as follows. The rate of loss of mass of component i in phase ϕ of tank Θ into stream s can be written using the chain rule of differentiation as

$$\left. \frac{dM(\Theta, i, \phi)}{dt} \right|_{out, s} = \frac{dM(\Theta, i, \phi)}{dV^{\phi, s}} \frac{dV^{\phi, s}}{dV^s} \frac{dV^s}{dt} \quad (5.3)$$

where M is the mass, V is volume, and t is time. The superscript ϕ on V indicates the volume occupied by phase ϕ , and the superscript s indicates that it is the volume entering stream s . The second term is the ratio of volume of phase ϕ that becomes part of the volume entering the stream s . This is the volume $V^{\phi, s}$ multiplied by $\psi(\phi, s)$ and divided by the sum of such

products for all three phases. Therefore, it is the relative values of VOLSEP for the different phases that determines the access to the stream, and not the absolute values, because these are normalized by the division.

The right side of Equation (5.3) can be rewritten

$$= \frac{M(\Theta, i, \phi)}{V^{\phi, s}} \frac{\psi(\phi, s) V^{\phi, s}}{\sum_{\phi} \left\{ \psi(\phi, s) V^{\phi, s} \right\}} F(s) \quad (5.4)$$

where $\psi(\phi, s)$ is the VOLSEP value, and $F(s)$ is the volumetric flow rate of stream s . The volumes of the individual phases are given by

$$V^{\phi, s} = \frac{1}{\rho(\Theta, \phi)} \sum_i M(\Theta, i, \phi) \quad (5.5)$$

where $\rho(\Theta, \phi)$ is the density of phase ϕ in tank Θ . Therefore, it is convenient to define a variable

$$\Gamma(s, \phi) = \frac{\psi(s, \phi)}{\sum_{\phi'} \left\{ \frac{\psi(s, \phi')}{\rho(\Theta, \phi')} \sum_i M[\Theta(s), i, \phi'] \right\}} \quad (5.6)$$

The variable $\Gamma(s, \phi)$ is maintained in the simulation as the array PHASESEP (stream, phase) and must be recalculated every time mass balance calculations are made because it includes values of mass, M , that continuously change. Using this variable, the rate of loss of mass from a tank due to mass flow into streams can be written

$$\left. \frac{dM(\Theta, i, \phi)}{dt} \right|_{\text{out}} = \sum_s^{\text{out}} M(\Theta, i, \phi) \Gamma(s, \phi) F(s) \quad (5.7)$$

where the summation is over all streams that are flowing out of the tank.

5.3 SEDIMENTATION AND RESUSPENSION

Sedimentation of the undissolved solids phase, a hypothetical departure from ideal process behavior, is addressed by defining a coefficient, α_S , with units of volumetric flow rate. This coefficient is the ratio of mass loss from liquid by sedimentation to the mass concentration of the undissolved solids phase (Phase 3) in the liquid. That is,

$$\frac{dM(\Theta, i, 4)}{dt} = - \left. \frac{dM(\Theta, i, 3)}{dt} \right|_{\text{settling}} = \alpha_S \frac{M(\Theta, i, 3)}{V_{\text{mix}}} \quad (5.8)$$

where Phase 4 is the settled phase, and V_{mix} is the volume of the phases constituting the mixed liquid; that is, Phases 1, 2, and 3.

The complementary process of resuspension of sedimented solids is described by a coefficient, α_R , with units of inverse time that defines the ratio of rate of loss of mass from the sediment phase (Phase 4) to the mass of the sediment phase. That is,

$$\left. \frac{dM(\Theta, i, 3)}{dt} \right|_{\text{resuspend}} = - \frac{dM(\Theta, i, 4)}{dt} = + \alpha_R M(\Theta, i, 4) \quad (5.9)$$

5.4 CAKING

Caking of both dissolved and undissolved solids on the sides of tanks above the liquid level is another hypothetical departure from ideality addressed by the simulation. Rates of loss or gain of mass to the mixed volume (Phases 1, 2, and 3) in a tank are computed as follows.

If the liquid level in a tank is decreasing, Phases 2 and 3 (dissolved and undissolved solids) are assumed to be left behind on the wall of the tank (as though by drying at the liquid meniscus) at a rate described by a dimensionless coefficient α_C . The coefficient is the ratio of the rate of loss of mass to the product of the mass of phases 2 and 3 and the rate of change of volume in the tank divided by the mixed volume in the tank. That is,

$$\left. \frac{dM(\theta, i, \phi)}{dt} \right|_{\text{caking}} = - \alpha_c \frac{dV}{dt} M(\theta, i, \phi) / V^m, \quad \phi = 2 \text{ or } 3 \quad (5.10)$$

where V is the volume of mass in the tank and V^m is the combined volume of the mixed Phases 1, 2, and 3. The terms V and V^m differ only in that the V corresponds to the liquid level and includes the volume, if any, of Phase 4, sediment, because this phase affects the liquid level in the tank. For the case of decreasing liquid level, the time derivative of the mass $M(\theta, i, 5)$, the caked phase, is the negative of the sum of the time derivatives for Phases 2 and 3.

For the case of increasing liquid level in a tank, the mass of Phase 5 is assumed to be redistributed to Phases 2 and 3 in accordance with the term $\Omega(\theta, i, \phi)$ described above, and at a rate depending on the rate of increase of liquid level and on the height of cake on the walls of the tank. The height is assumed to correspond to the highest volume ever occurring in the tank. It is stored as a variable called HIGHVOL, which is continuously updated for each tank during the simulation. Although presumably not accurate, for the sake of tractability, we assume that the mass deposited as cake is homogeneous and can be described without reference to a vertical distribution of composition within the cake. Assuming also that the cake is returned to the liquid as it is touched by rising liquid, the rate of return of mass to the liquid is described by

$$\left. \frac{dM(\theta, i, \phi)}{dt} \right|_{\text{return cake}} = - \Omega(\theta, i, \phi) \frac{dM(\theta, i, 5)}{dt} \quad (5.11)$$

where

$$\frac{dM(\theta, i, 5)}{dt} = - \frac{dV/dt}{V' - V} M(\theta, i, 5) \quad (5.12)$$

and where V' is the highest liquid level (expressed in terms of liquid volume) that has occurred in the tank.

6.0 EXAMPLE APPLICATION OF METHODS TO WVDP

To evaluate the ability of the methods described in Sections 4.0 and 5.0 to simulate a vitrification process, they were applied to the case of a system patterned roughly after the WVDP at West Valley, New York. The PNL simulation is not of this exact process, because parts of the process and the control strategy are still being determined. Instead, we have included some of the essential features of the process and plausible values for the simulation parameters in order to test the simulation methods.

Since estimates of initial masses in tanks were obtained in units of kilograms, estimates of flow rates and tank volumes were obtained in units of gallons per minute. Since we considered "hours" to be the most convenient unit of time for the simulation, we adopted the nonstandard set of units kilogram-gallon-hour for the simulation. Hence, densities were estimated in units of kilograms per gallon.

The process that was simulated is depicted in Figure 6.1, and is as follows.

FIGURE 6.1. Schematic of LFCM Vitrification System Patterned Generally After the West Valley System

6.1 TANKS

Nine process tanks are simulated, including:

- a "waste" tank containing the waste to vitrified
- a "concentrator/feed make-up tank" (CFMUT) where waste is sampled, concentrated by evaporation, and adjusted by adding chemical components to create a batch of feed for the melter
- a "melter feed tank" (MFT) where the feed is received from the CFMUT, sampled, and held as it is fed continuously to the melter, or until it is rejected and transferred back to the waste tank if the results of sampling the tank's contents show the feed composition to be unacceptable
- the melter is described as two tanks: the "cold cap," where melter feed resides while it volatilizes or melts, and the "glass," which is the pool of molten glass in the melter. The cold cap is treated as though no mass accumulates and therefore is not included in transient mass balance calculations. Instead, the mass flows of components into and out of the tank are balanced in accordance with specifications on how components in inlet streams distribute to phases and how phases are accessed by outlet streams. A melter is where feed is split into nonvolatile components that enter the glass, and volatile components that exit to the off-gas system.
- a "canister" into which glass from the "glass" tank pours or is airlifted. The only mass sent to the tank is from Phase 3 of the cold cap via the glass "tank," and Phase 3 of the canister is the only phase in the canister that contains mass.
- a "submerged bed scrubber" (SBS) that captures 20% of the volatilized water from the melter and any nonvolatiles entrained in the off-gas stream, and which passes the remaining 80% of the water on through the off-gas system. The mass captured by the SBS is from Phase 2 of the cold cap. The mass distributes among phases as for the slurry tanks.

- a CFMUT condensate tank that collects water evaporated from the CFMUT
- a fictitious "off-gas" tank that represents the accumulation of the off gas exiting the SBS.

The physical meanings attached to the phases in the tanks are presented in Table 6.1.

The density of Phase 1 is that of liquid water. The density of Phase 3 is a rough estimate of the density of solids in a slurry. The density of Phase 2 is a rough estimate of the density of dissolved solids, which in fact

TABLE 6.1. Simulated Tanks and Physical Meaning of Phases

<u>Tank Name</u>	<u>Phase 1</u>	<u>Phase 2</u>	<u>Phase 3</u>
Waste	water	dis. solids	undis. solids
CFMUT	water	dis. solids	undis. solids
MFT	water	dis. solids	undis. solids
Cold Cap	uncondensibles	condensibles + entrained solids	nonvolatiles
Glass	[not used]	[not used]	glass
SBS	water	dis. solids	undis. solids
Off gas	water	uncondensibles	[not used]
CFMUT Condensate	water	[not used]	[not used]
Canister	[not used]	[not used]	glass

For all tanks the densities of the phases are assumed to be:

phase 1	3.79 kg/gallon
phase 2	11.11 "
phase 3	11.11 "
phase 4	11.11 "
phase 5	[density not used in simulation]

was estimated to be approximately the density of Phase 3. The density of glass was taken to be that of Phase 3. The density of "solids" was estimated from a nominal slurry density and kilograms of oxides per gallon, and hence includes volatiles such as nitrate. Volatiles other than water have not been considered as separate components in the simulation.

6.2 STREAMS

The names of the process streams, their relation to the tanks, and their assumed flow rates ("gph" signifies gallons per hour) are:

- "Waste to CFMUT," transferring waste from the waste tank to the CFMUT in batches (6000 gph)
- "CFMUT to MFT," transferring melter feed from the CFMUT to the MFT in batches (6000 gph)
- "MFT to melter," continuously transferring melter feed from the MFT to the melter (cold cap) (30 gph)
- "Melting," representing the transfer of nonvolatiles from the "cold cap" to the "glass" (flow rate calculated to maintain zero accumulation in Phase 3 of cold cap)
- "SBS capture," representing the transfer of water and entrained nonvolatiles from the cold cap that are captured by the SBS (flow rate calculated to maintain zero accumulation in Phases 1 and 2 of cold cap)
- "Off gas," representing the transfer of water and volatiles from the cold cap that pass through the SBS to the off-gas system (flow rate calculated to maintain zero accumulation in phase 1 of cold cap)
- "SBS to CFMUT," transferring the accumulated contents of the SBS to the CFMUT in batches (3000 gph)
- "CFMUT evaporation," transferring evaporating water from the CFMUT to the CFMUT condensate tank (125 gph as liquid)

- "CFMUT to waste," transferring part of the contents of the CFMUT back to the waste tank if required in order to add chemicals with a slurry of acceptable solids loading (6000 gph)
- "MFT to waste," rejecting the contents of the MFT to the waste tank if sampling shows that an unacceptable feed has been made (6000 gph)
- "Glass airlift," transferring of glass from the "glass" tank to the "canister" tank by airlift (200 gph)
- "Glass overflow," transferring of glass from the "glass" tank to the "canister" tank by gravity overflow (flow rate calculated based on volume of glass in tank "glass" to simulate continuous overflow whenever the glass level is above a cutoff level).

6.3 CHEMICAL COMPONENTS

Eight chemical components have been assumed for the simulation. At this point, water is the only volatile component; all components except water become part of the glass. The components, their assumed target weight fractions in the glass, and their assumed initial masses in the waste tank are:

<u>Component</u>	<u>Target wt. fr.</u>	<u>Initial Mass in Waste Tank, 10⁴ kg</u>
1. Water	0.00	194
2. Silicon Dioxide	0.51	7.8
3. Sodium Oxide	0.12	7.7
4. Ferric Oxide	0.11	14.1
5. Boron Oxide	0.10	0.33
6. Aluminum Oxide	0.07	0.45
7. Potassium Oxide	0.04	0.18
8. Thorium Oxide	0.04	4.2
9. "Fission Products"	0.01	0.13

6.4 PROCESS CONTROL STRATEGY

An understanding of the WVDP process control strategy has been developed through a number of informal discussions with cognizant staff. A strategy for controlling the WVDP vitrification process was constructed that is thought to roughly simulate the actual process. We have not attempted to simulate the WVDP faithfully; instead, we assume the simulated construction is close enough to the WVDP facility for realistic tests. Probably the most significant departure from our understanding of the WVDP strategy is that we have included an additional sampling step, as discussed below.

The salient features of our control strategy are:

1. Liquid is sent from the SBS to the CFMUT if the measured liquid volume in the SBS has exceeded a specified level.
2. Waste is transferred from the waste tank to the CFMUT whenever the measured liquid volume in the CFMUT is low enough and provided any need to send liquid from the SBS has been satisfied.
3. After the CFMUT is filled from the SBS and waste tank, the contents are sampled, the amount of volume to be removed by evaporation is computed, and evaporation begins.
4. When the evaporation is complete as determined by measuring the volume in the CFMUT, chemicals are added to create a feed that will become glass of the target composition, with enough water added to achieve a desired solids loading in the feed. The chemicals and water are assumed to be added in the form of a slurry; if the solids loading of the slurry would exceed a specified limit, part of the contents of the tank are sent back to the waste tank, and a new computation of chemicals to be added is made.
5. After addition of chemicals is complete, a sample is taken. This is believed to be a departure from current WVDP plans, but was included to simplify (in the simulation) recording the contents of the CFMUT following the addition of chemicals.
6. Once both the chemical addition cycle in the CFMUT has been completed and the volume of liquid in the MFT has decreased to a

specified level, feed is transferred from the CFMUT to the MFT until either the liquid volume in the CFMUT has decreased to a specified level or the liquid volume in the MFT has increased to a specified level.

7. The contents of the MFT are sampled. If allowed (see below), feed is sent to the melter. Once the MFT sample results are available they are checked to see if the contents are acceptable. If not, melter feeding is stopped, the contents are rejected to the waste tank, and the MFT waits for a replacement batch from the next CFMUT cycle.
8. Feeding the melter is disallowed if the liquid volume in the SBS exceeds a specified level, if melting is disallowed (see below), or if feed is not available from the MFT.
9. Melting is disallowed if the volume of glass in the melter is too high and a canister is not in place.
10. Glass pours from the melter to the canister by overflow whenever the glass volume exceeds a pouring threshold.
11. When the volume of glass in the canister reaches a specified level, glass is airlifted from the melter to the canister for a specified period. After the airlift is complete, a new canister is installed.

The implementation of this strategy in terms of a "case" input file is presented in the form of an annotation of the input file that was used in a trial application of the model. The annotated file is presented in Appendix A, "Annotated Case Input File for Control of Process Similar to WVDP Process."

The simulation described in this section was compiled in VAX Fortran 4.5 and implemented using a MicroVax II computer with a "D" floating point CPU and 10MB of memory. Using this system, the simulated process time advanced 200 times faster than the computation time.

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7.0 METHODS FOR MULTIVARIATE STATISTICAL ANALYSIS OF PROCESS DATA

7.1 INTRODUCTION

The first two elements of the NWTP approach to waste form qualification, simulating the process and introducing departures from ideal behavior, have been discussed. This section and several appendices address the third element: analyzing simulated process data as we would real data to determine the effectiveness of statistical process control methods to monitor and control the process. Since the actual glass composition is known from the simulation, we can observe the impact of simulated departures from ideal behavior on the composition of the glass.

The analyses presented in this section demonstrate the multivariate process control methods described in Appendix B. The multivariate control charts are of the Shewhart type and are effective tools for detecting sudden, large shifts in the process average. Another type of control chart that can be constructed using the Hotelling T^2 statistic is the cumulative sum (CUSUM) control chart, which is effective for detecting small shifts from the process target. CUSUM control charts, along with control charts that monitor the variation of the process (i.e., assure that the uncertainty remains constant), are not demonstrated but may prove useful during operation of an LFCM.

The results of analyzing the simulation data are divided into two sections. First, the control charts for the unperturbed data are given. Second, the same results are given for the perturbed data. With the results in these two sections, the methods outlined in Appendix B are demonstrated and their merits illustrated.

Within the two sections, the results are given for two different control schemes. One scheme uses the traditional approach of using within-batch variation to control all batch-to-batch differences to zero. The second scheme allows some batch-to-batch variation. Determining which of these two control schemes is most applicable to a given process depends upon the objective of the process control.

7.1.1 Statistical Process Control Methods

In an industrial process the causes for deviations from a target are the collective result of assignable causes and chance fluctuations. The chance fluctuations result from all the slight causes that occur throughout a process and that cannot be traced to a specific source, and cannot be corrected without revising the whole process. The assignable causes are the traceable causes that can be corrected without causing the process to deviate from its target. Statistical process control methods seek to separate the assignable causes from the chance or random fluctuations by determining the distribution of the random fluctuations, then declaring anything outside of the distribution to be an assignable cause. As a result, the only assignable causes left are those that cannot be distinguished from the chance fluctuations.

For the vitrification system, the fluctuations introduced through sampling and analyses define as the acceptable variation of the process. The assignable causes are those sources of process variation that cause the process to deviate from its target by an amount greater than the sampling and analytical errors. This control scheme tends to control batch-to-batch differences to zero.

For this study, a second type of control scheme that permits some random fluctuations in selected assignable causes was also demonstrated. In most industrial applications, random fluctuations are unacceptable because the parts being manufactured must be as homogeneous as possible. However, in the vitrification process, the batches of glass are not required to be exactly the same. The compositions of glass batches need to be within a region that is acceptable for a radioactive waste glass; thus, some degree of batch-to-batch variation is acceptable. It is possible to control the composition of the glass to be within a region about a target composition vector, if the control scheme is based on batch variations in addition to sampling and analytical variations. The data from the simulated LFCM runs actually showed random variations between the batches, so for this particular data it is appropriate to include some batch-to-batch variation in the

control scheme. The two schemes are distinguished by indicating whether or not the batch covariance matrix is included in the calculations.

The process control statistics are calculated as if these simulated runs were the first runs from which data are gathered. As the data from each batch becomes available, the covariance matrices are re-estimated using all previously collected information. This method is followed to obtain a precise estimate of the covariance matrices. Thus, the sensitivity of the control charts increases as the number of batches increases. However, if precise estimates of the covariance matrices are available from previously collected data, it is not necessary to follow this method. The difference between an estimate of the covariance matrices based on previously collected data and re-estimating the covariance matrices as the runs progress is shown for the perturbed data.

7.1.2 Data Used

The process as described in Section 6.0 was simulated without and then with the addition of two departures from ideal behavior. The simulations were designated run B1035 and B1617, respectively, and the resulting data sets are termed "perturbed" and "unperturbed" in this report.

The departures from ideality for run B1617 were inclusion of a bias of +250 gallons in the volume measurement at the concentrator/feed makeup tank (CFMUT) at 600 hours simulated time, and inclusion of a precipitation/resuspension process in the melter feed tank (MFT) at 1200 hours simulated time. Precipitation in the MFT was simulated as though it occurred constantly, with the parameter α_S of Section 5.3 set at 3 gallons per minute. Resuspension was simulated as though it occurred only when the MFT was being filled, with the parameter α_R of Section 5.3 set at 0.5/hour. The methods outlined in Appendix B and G were used to analyze the data from these two runs.

The simulated data are composed of concentration measurements on eight oxides and measurements of several process variables. The eight oxides were SiO_2 , Na_2O , Fe_2O_3 , B_2O_3 , Al_2O_3 , K_2O , ThO_2 , and fission products. The process variables were full tank volumes and heel tank volumes for both the CFMUT and MFT, the times when those volumes were reached, batch number, sample number,

analysis number, number of samples per batch, number of analyses per sample, melter volume, and times of glass pours from the melter into canisters.

The oxide concentrations were calculated from the "slurry density" and the measured weight fractions for each oxide for each analysis. The "slurry density" is the mass of glass components in the slurry per volume of slurry. In the case of glass slurry, the "slurry density" is the density of the glass. But in the case of the waste/frit slurry in the CFMUT and MFT, it is less than the density of the waste/frit slurry. The "slurry density" was measured for each sample, so it is constant for each of the analyses done on that sample. The oxide concentrations for each component for each analysis is equal to the product of the observed sample "slurry density" and the observed weight fraction for each analysis.

Heel volume fractions for both tanks are equal to the heel volume of the previous batch divided by the full tank volume of the current batch. For example, the heel volume fraction of the third batch is equal to the heel volume from the second batch divided by the full volume of the third batch. These heel volume fractions were calculated for both the CFMUT and the MFT.

The difference between the time when the full tank volume was reached and the time when the heel volume was reached was used as the time duration of a batch. The difference between the full MFT volume and the MFT heel volume divided by the time duration of the corresponding batch was used as the volumetric flow rate from the MFT to the melter. These batch durations and batch volumetric flow rates were used to predict the composition of the melter glass.

The "clean" run continued for 2400 hours and resulted in 25 CFMUT batches and 24 MFT batches. For both tanks there were three samples per batch and three analyses per sample. Sixty-eight glass pours were made during the run, which equals about 1 to 4 pours per batch. One sample per pour and three analyses per sample were obtained.

The "perturbed" run continued for 2300 hours and resulted in 23 CFMUT batches and 22 MFT batches. Again, there were three samples per batch and

three analyses per sample for both tanks. Sixty-eight glass pours were made during the run. One sample per pour and three analyses per sample were obtained.

7.1.3 Application of Statistical Methods

Both the unperturbed and perturbed data sets are analyzed using the methods outlined in Appendix B. For the unperturbed data set, multivariate process control charts are given for the CFMUT, MFT, transfer of waste/frit slurry from the CFMUT to the MFT, combined estimate of the MFT composition based on the data from the CFMUT and MFT, and predicted glass composition in the melter. Also, the increased precision that results from combining the CFMUT and MFT data into a single estimate of the MFT composition is shown. Examples of the discriminant function, simultaneous confidence intervals, and Bonferroni confidence intervals are given for the elements of a single batch mean vector. In the case of the perturbed data set, multivariate control charts are given for the CFMUT, MFT, and the transfer of waste/frit slurry from the CFMUT to the MFT. The capability to vary the sensitivity of the multivariate control chart by allowing different batch variabilities is demonstrated for the CFMUT. As in the case of the unperturbed data, examples of the discriminant function, simultaneous confidence intervals, and Bonferroni confidence intervals are given for the elements of a single batch mean vector.

7.2 ANALYSIS OF THE UNPERTURBED DATA

The process control charts and batch mean vector estimates are demonstrated for the CFMUT, MFT, transfer of material from the CFMUT to the MFT, combined estimates of the MFT composition, and predicted glass composition in the melter.

To construct a control chart, the vector of the target compositions is subtracted from the vector of estimated mean compositions. The resulting vector of differences is then scaled so that the distance from the estimated batch mean vector to the target vector is expressed in terms of the average uncertainty due to the random fluctuations. If the process is in statistical control, then this statistic will have the Hotelling T^2 distribution and will

fall within the limits of the distribution. The control limits used in this demonstration are such that only 0.1% of the distribution is outside of the limits (100% coverage requires infinite limits). If the process is out of statistical control, the observed value of the statistic will fall outside of the distributional or control limits and it is concluded that the true batch composition differs significantly from the target composition. In this demonstration two types of distributions are used, one with a linear function of the covariance matrices for sampling and analyses as the measure of average uncertainty, and another with a linear function of the covariance matrices for batches, sampling, and analyses as the measure of average uncertainty.

For the purpose of this demonstration, it is assumed that the amount of batch-to-batch variation introduced during the simulation is the a priori desired amount of such variation (i.e., the control scheme that permits random fluctuations in selected assignable causes). Since real batch-to-batch random fluctuations were included in the simulation, the first type of control scheme will always appear to be too sensitive or out of statistical control.

The control charts show that the critical values decrease as the number of batches increase. Since no previous information is available, the estimates of the covariance matrices are based on all previously collected data. Therefore, as additional data become available, more precise estimates of the covariance matrices are obtained. (All the Hotelling T^2 statistics calculated for each batch are correlated such that tests for the number of batches above or below the target are not applicable.)

7.2.1 CFMUT Control Charts

Figure 7.1 illustrates the process control chart for the CFMUT composition based on Hotelling T^2 statistics when no batch covariance matrix is included in the control scheme. Since the data actually contain some random batch-to-batch variation, most of the batch mean vectors are shown to be greater than their corresponding critical values. Figure 7.2 is the same control chart, but includes the batch covariance matrix. The Hotelling T^2 statistics were calculated using Equation (B.2.12) in Appendix B. (The

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FIGURE 7.1. Multivariate Control Chart for CFMUT Batch Mean Vectors for the Unperturbed Data. Batch-to-batch covariance matrix is not included. (Extremely large initial critical values set equal to 1300. First 4 batches are 0.0 because of insufficient data to calculate statistic.)

statistics for Figure 7.1 were obtained by setting the batch covariance matrix in that equation equal to a matrix of zeros.) Based on Figure 7.2, the process is not deemed out of control. Figures 7.1 and 7.2 illustrate the difference between the sensitivities of the two types of control schemes. For this demonstration, Figure 7.2 is the correct control chart.

Note that the control charts start for different batches. This is because the covariance matrices cannot be estimated until certain amounts of data are available, and these amounts differ for the three kinds of covariance matrices used in these statistics. If the batch covariance matrix is included in the control scheme, then the number of batches needed before the batch covariance matrix can be estimated must be at least the number of constituents, plus two. If the batch covariance matrix is excluded from the control scheme, then the number of batches times the number of samples minus one, $b(s-1)$, must be greater than the number of constituents.

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FIGURE 7.2. Multivariate Control Chart for CFMUT Batch Mean Vectors for the Unperturbed Data. Batch-to-batch covariance matrix is included. (Extremely large initial critical values set equal to 234. First 9 batches are 0.0 because of insufficient data to calculate statistic.)

7.2.2.1 CFMUT Example Batch

In Table 7.1 the sample discriminant function, simultaneous confidence intervals, Bonferroni confidence intervals, estimated batch mean vector, target composition vector, standard deviation of the elements of the estimated batch mean vector, and those same standard deviations in percent relative standard deviation form (relative to the target vector) are given for batch 14 for both control schemes. None of the confidence intervals indicate that any of the oxide concentrations are significantly different from the target oxide concentrations.

7.2.2.2 Discriminant Function

The discriminant function is the vector of coefficients for the linear combination of the oxide concentrations that maximizes the Hotelling T^2

TABLE 7.1. Discriminant Function, Simultaneous Confidence Intervals ($\alpha = 0.001$), Bonferroni Confidence Intervals ($\alpha = 0.001/16$), Estimated Batch Means, Target Means, Standard Deviation of the Estimated Batch Means and %RSD = $100 \times \text{sd}(\text{mean})/\text{target}$ for Batch 14 of the "Unperturbed" CFMUT Data. Prefixes "u" and "l" distinguish upper and lower confidence interval limits. For each batch these statistics are calculated with and without including the batch-to-batch variability. Also, the Hotelling T^2 statistic along with its critical value is given.

Batch 14								
Without Batch to Batch Variability								
	SiO ₂	Na ₂ O	Fe ₂ O ₃	B ₂ O ₃	Al ₂ O ₃	K ₂ O	ThO ₂	FsnPrd
dscrm	-142.63	-1761.9	-325.97	-1017.5	-712.62	-5474	1570.73	1968.56
usmltns	1.0673050	0.2249808	0.2223543	0.1851325	0.1402880	0.0746067	0.0816305	0.0191075
ubnfrn	0.9827437	0.2136534	0.2071304	0.1767527	0.1312383	0.0718643	0.0758976	0.0182777
mean	0.8417999	0.1947732	0.1817558	0.1627857	0.1161547	0.0672934	0.0663421	0.0168946
target	0.8772000	0.2064000	0.1892000	0.1720000	0.1204000	0.0688000	0.0688000	0.0172000
lbnfrn	0.7008560	0.1758930	0.1563813	0.1488187	0.1010710	0.0627224	0.0567866	0.0155116
lsmltns	0.6162947	0.1645655	0.1411574	0.1404390	0.0920213	0.0599800	0.0510537	0.0146818
sd(mean)	0.0299705	0.0040147	0.0053957	0.0029700	0.0032074	0.0009720	0.0020319	0.0002941
%rsd	3.4166114	1.9451141	2.8518456	1.7267262	2.6639644	1.4127492	2.9533299	1.7098707
Hotelling T^2 Statistic = 44.15 Critical Value = 56.61 Degrees of Freedom = 28 $\alpha = 0.001$								
With Batch to Batch Variability								
	SiO ₂	Na ₂ O	Fe ₂ O ₃	B ₂ O ₃	Al ₂ O ₃	K ₂ O	ThO ₂	FsnPrd
dscrm	-278.59	-451.49	1028.38	-996.41	-1462.9	1594.74	409.77	11679
usmltns	1.4828624	0.4113547	0.3500352	0.2749003	0.2086345	0.1070456	0.1437425	0.0306898
ubnfrn	1.0462654	0.2638514	0.2354282	0.1985444	0.1456509	0.0799723	0.0910288	0.0212946
mean	0.8417999	0.1947732	0.1817558	0.1627857	0.1161547	0.0672934	0.0663421	0.0168946
target	0.8772000	0.2064000	0.1892000	0.1720000	0.1204000	0.0688000	0.0688000	0.0172000
lbnfrn	0.6373343	0.1256950	0.1280835	0.1270270	0.0866584	0.0546145	0.0416554	0.0124947
lsmltns	0.2007373	-0.0218083	0.0134765	0.0506712	0.0236748	0.0275411	-0.0110583	0.0030995
sd(mean)	0.0352969	0.0119250	0.0092654	0.0061730	0.0050919	0.0021888	0.0042617	0.0007596
%rsd	4.0238108	5.7775995	4.8971719	3.5889653	4.2291830	3.1813325	6.1942758	4.4160417
Hotelling T^2 Statistic = 15.87 Critical Value = 329.9 Degrees of Freedom = 13 $\alpha = 0.001$								

statistic. No other linear combination of the estimated batch concentrations will deviate further from the same linear combination of the target concentrations. The magnitude of these coefficients is mainly a function of the magnitude of the corresponding oxide's variance, and the magnitude of its deviation from its target value. If the estimated batch mean vector exactly equals the target vector, then the coefficients will be zero. The larger the coefficient of a particular oxide, the more sensitive the process control scheme is to deviations of that oxide from its target value for that particular batch. The discriminant function will be different for each batch.

The discriminant function for batch 14 without the batch covariance matrix indicates that the Hotelling T^2 statistic is most sensitive to deviations of K_2O from its target, followed by the fission products Na_2O , ThO_2 , B_2O_3 , K_2O , Al_2O_3 , Fe_2O_3 and B_2O_3 . When the batch covariance matrix is included, fission products are least able to deviate from their target without causing the batch to be out of control. The statistic is not relatively sensitive to the deviations of the other oxide concentrations from their target values for this batch. As processing continues, one can track the discriminant function to determine, on the average, those oxide concentrations to which the control scheme is most sensitive. Control of the process can then be enhanced by increased care in adding those oxides to the waste.

7.2.2.3 Confidence Intervals

Two types of confidence intervals can be used to report the batch mean estimates: simultaneous and Bonferroni intervals. Simultaneous confidence intervals are formed by taking the square root of the critical value of the Hotelling T^2 distribution, multiplying it by the standard deviations of the estimated means, and adding and subtracting the result from the estimated means. The standard deviations are the square roots of the main diagonal elements of the covariance matrix of the estimated batch mean vector. Bonferroni confidence intervals are formed in the same way, except the square root of the critical value of the Hotelling T^2 distribution is replaced by a critical value from the usual Student's t -distribution. The alpha level of

the Bonferroni intervals is the alpha level of the simultaneous interval, divided by twice the number of confidence intervals to be formed. ($1 - \alpha$ is the probability that the confidence interval will contain the true value of the composition.)

These intervals differ in that the simultaneous intervals are more conservative (i.e., wider) than the Bonferroni intervals. The simultaneous intervals are designed so that the multiple of the appropriate standard deviation is constant for any number of linear combinations of the estimated oxide concentrations. Regular confidence intervals based on Student's t-distribution could be constructed, but they would be too narrow. As more and more regular intervals at a fixed alpha level are calculated, the probability that one or more of the intervals will not contain the true value being estimated will increase until it reaches one. The simultaneous intervals are a solution to this problem for an infinite number of intervals; however, since researchers usually are only interested in a finite number of intervals, the simultaneous intervals are too wide. The Bonferroni intervals represent a compromise between the simultaneous and regular confidence intervals and will be closest to the correct intervals. Both simultaneous and Bonferroni intervals are given for comparison. Note that the simultaneous intervals are always wider than the Bonferroni intervals.

The process target and estimated batch mean concentration vector is given in Table 7.1. If the target concentration is inside the confidence intervals, it cannot be concluded that the true batch mean concentration for the corresponding oxide differs from the target concentration. However, additional data may provide the increased sensitivity required to distinguish between the two vectors.

Also given in Table 7.1 are the standard deviations and percent relative standard deviations for each of the oxides. The standard deviations are the square root of the variances of the mean oxide concentration estimates located on the main diagonal of the covariance matrix of the estimated means. The percent relative standard deviations are calculated by dividing the standard deviations of the means by their corresponding target values and multiplying by 100.

Table 7.1 shows that the confidence intervals are different, depending on whether or not the batch covariance matrix was included in the covariance matrix of the batch mean vector. Also, note that these differences are not constant across oxides. This reflects the different behaviors of the oxides in the simulation. For this particular batch, neither of the Hotelling T^2 statistics exceeded their critical values.

For the batch illustrated in Table 7.1, none of the target values fall outside the confidence intervals. This is true of all the simultaneous intervals for all the batches from the CFMUT unperturbed data. It is also true for all the Bonferroni intervals when the batch covariance matrix is included in the covariance matrix of the estimated batch mean vectors for the same data set. In addition, it is also true for most of the batch means where the batch covariance matrix was excluded from the covariance matrix of the batch mean vectors.

Note that the Hotelling T^2 statistic can still detect an out-of-control batch even if all of the individual confidence intervals contain their respective true composition values. This is because the Hotelling T^2 statistic is also testing all linear combinations of the differences between the estimated batch means and the true means for equality with zero. It is possible for the individual concentration estimates for oxides to be close enough to their corresponding target values that the individual differences do not appear to be significantly different from zero, but have linear combinations of the differences that are significantly different from zero. The process is in statistical control if all linear combinations of the differences are not significantly different from zero.

7.2.2 MFT Control Charts and Example

Figures 7.3 and 7.4 are the multivariate process control charts for the unperturbed data from the MFT. These plots are interpreted in the same manner as Figures 7.1 and 7.2. The only difference between the CFMUT and MFT data sets is that the MFT is characterized by a different set of random sampling and analytical errors. Therefore, essentially the same results are expected and obtained, although patterns of the plots are slightly different.

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FIGURE 7.3. Multivariate Control Chart for MFT Batch Mean Vectors for the Unperturbed Data. Batch-to-batch covariance matrix is not included. (Extremely large initial critical values set equal to 850. First 4 batches are 0.0 because of insufficient data to calculate statistic.)

This is because transferring material from the CFMUT to the MFT divides the CFMUT batches into new batches and heels in the MFT.

Table 7.2 contains the same statistics as Table 7.1 for the batch with the same sequential number. The batch/heel remixing of the waste/frit slurry in the MFT, along with a new set of sampling and analytical errors, causes only small differences in the numbers that are in the two tables.

Note that the standard deviation of the mean for SiO_2 is smaller when the batch covariance matrix is included in the covariance structure of the mean vector. This is because the estimate of the true batch covariance matrix is indefinite instead of positive definite like the true batch covariance matrix. If the true batch covariance matrix is not negligible, then the estimate of the true batch covariance matrix will converge to a positive definite matrix as the number of batches becomes arbitrarily large.

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FIGURE 7.4. Multivariate Control Chart for MFT Batch Mean Vectors for the Unperturbed Data. Batch-to-batch covariance matrix is included. (Extremely large initial critical values set equal to 234. First 9 batches are 0.0 because of insufficient data to calculate statistic.)

The indefinite estimate of the true batch covariance matrix was used to preserve the unbiased properties of the variance estimates and the control scheme.

7.2.3 Transfer of Waste/Frit Slurry from the CFMUT to the MFT

Figure 7.5 gives the multivariate process control chart for batch transfers of waste/frit slurry from the CFMUT to the MFT for the unperturbed data. To estimate the transfer of waste/frit slurry from the CFMUT to the MFT, estimates of the MFT batch mean vectors based on the CFMUT batch mean vectors were subtracted from the estimates of the MFT batch mean vectors based on the MFT data. There is only one possible covariance structure for this chart, so there are no comparing control schemes that include or exclude the batch covariance matrix. The Hotelling T^2 statistics were calculated per Equation B.3.9 in Appendix B. Based on this control chart, one concludes

[illegible]

FIGURE 7.5. Multivariate Control Chart for Differences Between MFT Batch Means and MFT Batch Means Predicted from CFMUT Batch Mean Vectors for the Unperturbed Data. (Large critical values set equal to 100. First 2 batches are 0.0 because of insufficient data to calculate the test statistic.)

that no anomalies occurred in the oxide composition of the waste/frit slurry as was transferred from the CFMUT to the MFT. For the simulated run, this was actually the case.

Table 7.3 gives the same statistics listed in Tables 7.1 and 7.2 for the difference between a CFMUT batch mean vector and MFT batch mean vector. Because the target is always zero, a target is not listed and percent relative standard deviation is not calculated. None of the individual confidence intervals for any of the batches showed any significant changes in the composition of the waste/frit slurry during the transfers.

It should be noted that the multivariate process control on the transfer of waste/frit slurry from the CFMUT to the MFT can begin before multivariate process control on either the CFMUT or the MFT because the batch covariance matrix cancels the covariance structure sets of data.

TABLE 7.3. Discriminant Function, Simultaneous Confidence Intervals ($\alpha = 0.001$), Bonferroni Confidence Intervals ($\alpha = 0.001/16$), Estimated Batch Means, Target Means, Standard Deviation of the Estimated Batch Means and $\%RSD = 100 \times \text{sd}(\text{mean})/\text{target}$ for the Difference Between the MFT Raw Means and MFT Means Predicted from the CFMUT Means for Batch 14 of the "Unperturbed" Data. Prefixes "u" and "l" distinguish upper and lower confidence interval limits. For each batch these statistics are calculated with and without including the batch-to-batch variability. Also, the Hotelling T^2 statistic along with its critical value is given.

	Batch 14							
	<u>SiO₂</u>	<u>Na₂O</u>	<u>Fe₂O₃</u>	<u>B₂O₃</u>	<u>Al₂O₃</u>	<u>K₂O</u>	<u>ThO₂</u>	<u>FsnPrd</u>
dscrm	-2.7051158	355.76	38.7134533	544.655	406.108	-1031.1	-335.98	140.94
usmltns	0.2279225	0.0381715	0.0424340	0.0279875	0.0300750	0.0060225	0.0175768	0.0024290
ubnfrn	0.1654950	0.0295077	0.0304156	0.0218121	0.0220791	0.0036688	0.0127005	0.0017258
diffnc	0.0092347	0.0078218	0.0003326	0.0063546	0.0020646	-0.0022226	0.0004949	-0.0000343
lbnfrn	-0.1470256	-0.0138642	-0.0297504	-0.0091030	-0.0179499	-0.0081140	-0.0117108	-0.0017944
lsmltns	-0.2094530	-0.0225279	-0.0417688	-0.0152784	-0.0259459	-0.0104677	-0.0165870	-0.0024975
sd(diff)	0.0360959	0.0050094	0.0069491	0.0035707	0.0046233	0.0013609	0.0028195	0.0004066
Hotelling T^2 Statistic = 9.1907 Critical Value = 36.706 Degrees of Freedom = 56 $\alpha = 0.001$								

7.2.4 Combined Estimate of the MFT Composition

The MFT composition can be estimated by using Equation (B.3.16) in Appendix B to combine the information in the CFMUT and MFT data sets. Figures 7.6 and 7.7 give the multivariate process control charts and are interpreted the same as Figures 7.3 and 7.4. Note the increased sensitivity displayed in Figure 7.6 over that of Figure 7.3.

Table 7.4 gives the same statistics as Table 7.2 for the same MFT batch. A comparison of Tables 7.2 and 7.4 reveals that the standard deviations of the estimated means are reduced significantly when the batch covariance matrix is excluded (i.e., set to zero) in Equation (B.3.14). Only a small decrease is observed when the batch covariance matrix is included in Equation (B.3.14). Table 7.5 summarizes these differences for each oxide, as well as the overall average improvement across all batches.

FIGURE 7.6. Multivariate Control Chart for MFT Batch Mean Vectors Based on the Combined Unperturbed Data from the CFMUT and MFT, Batch-to-batch covariance matrix is not included. (Extremely large initial critical values set equal to 234. First 4 batches are 0.0 because of insufficient data to calculate statistic.)

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FIGURE 7.7. Multivariate Control Chart for MFT Batch Mean Vectors Based on the Combined Unperturbed Data from the CFMUT and MFT. Batch-to-batch covariance matrix is included. (Extremely large initial critical values set equal to 234. First 9 batches are 0.0 because of insufficient data to calculate statistic.)

Table 7.5 shows that improved precision is achieved when the CFMUT composition estimates are combined with the MFT estimates, particularly when batch variations are excluded. This reduction is not constant across oxides because of the correlations between the oxides, the random nature of the simulation, and the role of each oxide in the simulation. Depending on the inclusion of the batch covariance matrix the standard deviations will decrease, as shown by the relationship between correlations and the data. Two sets of data for which the multivariate normal distribution is uncorrelated will behave as two independent sets of data, and combining them into a single estimate doubles the amount of information known about the quantity being estimated. If the two sets of data are correlated, they do not behave as two independent sets of data. Combining two correlated sets of data into a single estimate does not double the information because of information overlap between the two data sets. Therefore, the information

Without Batch to Batch Variability

	SiO ₂	Na ₂ O	Fe ₂ O ₃	B ₂ O ₃	Al ₂ O ₃	K ₂ O	ThO ₂	FsnPrd
dscrm	-55.957	-3475.8	-828.2	-2456.5	-1023.8	-9542.7	588.333	-10682
usmltns	0.9779613	0.2133915	0.2068497	0.1782451	0.1334553	0.0708707	0.0762600	0.0182018
ubnfrn	0.9286113	0.2065426	0.1973489	0.1733633	0.1271343	0.0690101	0.0724053	0.0176459
lsemean	0.8463564	0.1951272	0.1815133	0.1652265	0.1165988	0.0659088	0.0659803	0.0167194
target	0.8772000	0.2064000	0.1892000	0.1720000	0.1204000	0.0688000	0.0688000	0.0172000
lbnfrn	0.7641015	0.1837118	0.1656777	0.1570898	0.1060632	0.0628076	0.0595552	0.0157929
lsmltns	0.7147514	0.1768629	0.1561769	0.1522080	0.0997422	0.0609470	0.0557005	0.0152370
sd(mean)	0.0174908	0.0024274	0.0033673	0.0017302	0.0022403	0.0006594	0.0013662	0.0001970
%rsd	1.9939365	1.1760617	1.7797574	1.0059410	1.8607129	0.9585021	1.9857898	1.1454337

Hotelling T^2 Statistic = 98.869 Critical Value = 56.61 Degrees of Freedom = 28 alpha = 0.001

With Batch to Batch Variability

	SiO ₂	Na ₂ O	Fe ₂ O ₃	B ₂ O ₃	Al ₂ O ₃	K ₂ O	ThO ₂	FsnPrd
dscrm	68.9015389	-193.87	-161.14	374.395	226.298	-400.54	658.607	-6208.3
usmltns	1.1785458	0.3542632	0.2933420	0.2541310	0.1808185	0.0984515	0.1172459	0.0257114
ubnfrn	0.9522605	0.2458768	0.2171611	0.1935635	0.1370646	0.0762839	0.0823346	0.0195858
lsmean	0.8462874	0.1951177	0.1814843	0.1651987	0.1165739	0.0659025	0.0659851	0.0167170
target	0.8772000	0.2064000	0.1892000	0.1720000	0.1204000	0.0688000	0.0688000	0.0172000
lbnfrn	0.7403143	0.1443586	0.1458076	0.1368339	0.0960832	0.0555211	0.0496356	0.0138483
lsmltns	0.5140290	0.0359723	0.0696267	0.0762663	0.0523293	0.0333535	0.0147244	0.0077227
sd(mean)	0.0182941	0.0087625	0.0061589	0.0048966	0.0035373	0.0017921	0.0028224	0.0004952
%rsd	2.0855142	4.2454165	3.2552193	2.8468667	2.9379612	2.6048623	4.1023469	2.8792362

Hotelling T^2 Statistic = 0.1935 Critical Value = 329.9 Degrees of Freedom = 13 alpha = 0.001

TABLE 7.5. Comparison of Estimates for Standard Deviation of Oxides, Based on MFT Data Only and a Combination of CFMUT and MFT Data^(a)

Without batch-to-batch variability			
Oxide	Minimum value	Average	Maximum value
SiO ₂	0.5371	0.6297	0.6901
Na ₂ O	0.5368	0.6048	0.7210
Fe ₂ O ₃	0.5105	0.6012	0.6786
B ₂ O ₃	0.5958	0.6427	0.7316
Al ₂ O ₃	0.4605	0.5495	0.6092
K ₂ O	0.5321	0.5647	0.5916
ThO ₂	0.5088	0.5724	0.6326
FsnPrd	0.5251	0.5911	0.6555
-----	-----	-----	-----
Average	0.5258	0.5945	0.6638

With batch-to-batch variability			
Oxide	Minimum value	Average	Maximum value
SiO ₂	0.6177	0.7491	1.0145
Na ₂ O	0.9346	1.0069	1.0420
Fe ₂ O ₃	0.7417	0.8497	0.9895
B ₂ O ₃	0.8786	0.9135	0.9432
Al ₂ O ₃	0.4883	0.7028	0.7817
K ₂ O	0.8122	0.8598	0.8869
ThO ₂	0.8434	0.9371	1.1236
FsnPrd	1.0501	1.1156	1.3273
-----	-----	-----	-----
Average	0.7958	0.8918	1.0136

(a) Table entries are Std.(CFMUT + MFT)/Std.(MFT) for all batches of the unperturbed data.

obtained by combining the data ranges between 1 and 2 times the amount of information available from one of the data sets (see Table 7.5).

The small decrease observed in the standard deviations when the batch covariance matrix is included in the estimation process may suggest that combining the data from the CFMUT and MFT is not beneficial if the batch covariance matrix is used in the control and estimation methods. The gain in precision depends on the relationship between the size of the batch-to-batch variation and the size of the sampling and analytical variations. This relationship can be assessed when the LFCM is operating.

7.2.5 Predicted Composition for the Melter Glass

Figures 7.8 and 7.9 give the multivariate process control charts for the glass pours made from the melter, with and without the batch covariance matrix included in the scheme. The glass compositions were predicted using Equation (B.4.15) in Appendix B. The estimated MFT batch mean vectors, based

FIGURE 7.8. Multivariate Control Chart for Predicted Glass Pour Mean Vectors for the Unperturbed Data. Batch-to-batch covariance matrix is not included. (Large critical values set equal to 234. Insufficient data in batches 1-9 to calculate T^2 .)

FIGURE 7.9. Multivariate Control Chart for Predicted Glass Pour Mean Vectors for the Unperturbed Data. Batch-to-batch covariance matrix included. (Large critical values set equal to 234. Insufficient data in batches 1-9 to calculate T^2 .)

on the combined CFMUT and MFT data, were used for these predictions. The waste/frit slurry oxide concentrations discussed previously are the oxide concentrations for a volume of feed. The oxide concentrations needed for Equation B.4.15 are concentrations per volume of glass in the feed. Therefore, the MFT concentrations were multiplied by the ratio of the glass oxide density to the feed oxide density (i.e., 11.13/1.72).

Three glass pours were made during the mixing of the fourteenth MFT batch. The statistics are given in Table 7.6.

7.3 ANALYSIS OF THE PERTURBED DATA SET

7.3.1 CFMUT Control Charts and Example Batch

Figures 7.10 and 7.11 give the same control charts as those given in Figures 7.1 and 7.2. The usual sensitivities that result from including or excluding the batch covariance matrix are observed. A comparison of Figure 7.10 to Figure 7.1 shows a perturbation in the process; however, Figure 7.11

Without Batch to Batch Variability

Pour # 1. Time Pour Occurred After Start of Batch = 33.9 Hours. Duration of Batch = 108.6 Hours.

	SiO ₂	Na ₂ O	Fe ₂ O ₃	B ₂ O ₃	Al ₂ O ₃	K ₂ O	ThO ₂	FsnPrd
dscrm	29.1252147	-4.1487840	16.0032216	275.715	-45.936	384.299	-301.13	2690.19
usmltns	6.5155137	1.4221873	1.3815214	1.2032071	0.8861849	0.4785205	0.5052023	0.1217581
ubnfrn	6.2572549	1.3860058	1.3317243	1.1771581	0.8531216	0.4685699	0.4850339	0.1188196
glsmear	5.8267986	1.3256998	1.2487243	1.1337407	0.7980129	0.4519845	0.4514180	0.1139220
target	5.6763000	1.3356000	1.2243000	1.1130000	0.7791000	0.4452000	0.4452000	0.1113000
lbnfrn	5.3963423	1.2653938	1.1657243	1.0903232	0.7429041	0.4353992	0.4178020	0.1090243
lsmtns	5.1380835	1.2292124	1.1159272	1.0642743	0.7098408	0.4254486	0.3976336	0.1060858
sd(mean)	0.0915329	0.0128236	0.0176493	0.0092324	0.0117184	0.0035267	0.0071482	0.0010415
%rsd	1.6125453	0.9601347	1.4415789	0.8295018	1.5040959	0.7921677	1.6056044	0.9357164

Hotelling T^2 Statistic = 17.453 Critical Value = 56.61 Degrees of Freedom = 28 alpha = 0.001

Pour # 2. Time Pour Occurred After Start of Batch = 66.0 Hours. Duration of Batch = 108.6 Hours.

	SiO ₂	Na ₂ O	Fe ₂ O ₃	B ₂ O ₃	Al ₂ O ₃	K ₂ O	ThO ₂	FsnPrd
dscrm	8.9685622	-210.16	-69.048	-42.139	-59.532	-434.52	-94.977	810.748
usmltns	6.4643881	1.4120245	1.3688655	1.1853085	0.8812322	0.4713505	0.5030274	0.1206187
ubnfrn	6.1700386	1.3711173	1.3121806	1.1560807	0.8435359	0.4602061	0.4800393	0.1172975
glsmear	5.6794278	1.3029347	1.2177001	1.1073650	0.7807051	0.4416311	0.4417236	0.1117619
target	5.6763000	1.3356000	1.2243000	1.1130000	0.7791000	0.4452000	0.4452000	0.1113000
lbnfrn	5.1888170	1.2347520	1.1232196	1.0586493	0.7178744	0.4230561	0.4034079	0.1062262
lsmltns	4.8944675	1.1938448	1.0665346	1.0294215	0.6801781	0.4119117	0.3804198	0.1029050
sd(mean)	0.1043243	0.0144985	0.0200905	0.0103590	0.0133604	0.0039498	0.0081475	0.0011771
%rsd	1.8378921	1.0855398	1.6409766	0.9307272	1.7148546	0.8872021	1.8300783	1.0576049

Hotelling T^2 Statistic = 9.746 Critical Value = 56.61 Degrees of Freedom = 28 alpha = 0.001

TABLE 7.6. (contd)

Pour # 3. Time Pour Occurred After Start of Batch = 99.8 Hours. Duration of Batch = 108.6 Hours.

	SiO_2	Na_2O	Fe_2O_3	B_2O_3	Al_2O_3	K_2O	ThO_2	FsnPrd
dscrm	2.7391796	-268.39	-90.714	-135.74	-64.037	-670.54	-32.454	201.22
usmltns	6.4624298	1.4107532	1.3674526	1.1804352	0.8815824	0.4693698	0.5035657	0.1203959
ubnfrn	6.1480175	1.3671100	1.3069193	1.1493127	0.8413123	0.4575071	0.4790077	0.1168534
glsmean	5.6239666	1.2943673	1.2060245	1.0974388	0.7741916	0.4377347	0.4380753	0.1109489
target	5.6763000	1.3356000	1.2243000	1.1130000	0.7791000	0.4452000	0.4452000	0.1113000
lbnfrn	5.0999157	1.2216245	1.1051297	1.0455650	0.7070709	0.4179623	0.3971429	0.1050445
lsmltns	4.7855034	1.1779814	1.0445963	1.0144425	0.6668008	0.4060996	0.3725848	0.1015020
sd(mean)	0.1114350	0.0154681	0.0214544	0.0110305	0.0142727	0.0042044	0.0087039	0.0012555
%rsd	1.9631628	1.1581416	1.7523832	0.9910638	1.8319416	0.9443911	1.9550607	1.1280635

Hotelling T^2 Statistic = 20.174 Critical Value = 56.61 Degrees of Freedom = 28 alpha = 0.001

With Batch to Batch Variability

Pour # 1. Time Pour Occurred After Start of Batch = 33.9 Hours. Duration of Batch = 108.6 Hours.

	SiO_2	Na_2O	Fe_2O_3	B_2O_3	Al_2O_3	K_2O	ThO_2	FsnPrd
dscrm	-0.2440381	-63.716	15.3435940	15.1135462	-45.784	-19.302	36.1649252	915.095
usmltns	7.4793776	2.2004042	1.8479074	1.6157603	1.1376651	0.6277510	0.7290476	0.1624898
ubnfrn	6.2878110	1.5891701	1.4256095	1.2746164	0.8973902	0.5029194	0.5347048	0.1281307
glsmean	5.7297809	1.3029192	1.2278404	1.1148532	0.7848655	0.4444588	0.4436909	0.1120399
target	5.6763000	1.3356000	1.2243000	1.1130000	0.7791000	0.4452000	0.4452000	0.1113000
lbnfrn	5.1717508	1.0166682	1.0300714	0.9550899	0.6723408	0.3859981	0.3526770	0.0959490
lsmltns	3.9801843	0.4054341	0.6077734	0.6139461	0.4320659	0.2611666	0.1583342	0.0615900
sd(mean)	0.0963327	0.0494155	0.0341409	0.0275799	0.0194251	0.0100921	0.0157117	0.0027778
%rsd	1.6971036	3.6998709	2.7886019	2.4779800	2.4932778	2.2668592	3.5291384	2.4957487

Hotelling T^2 Statistic = 2.5244 Critical Value = 329.9 Degrees of Freedom = 13 alpha = 0.001

TABLE 7.6. (contd)

Pour # 2. Time Pour Occurred After Start of Batch = 66.0 Hours. Duration of Batch = 108.6 Hours.

	SiO_2	Na_2O	Fe_2O_3	B_2O_3	Al_2O_3	K_2O	ThO_2	FsnPrd
dscrm	5.7074450	-38.802	-16.249	28.6412897	4.8047938	-36.889	50.5406201	109.017
usmltns	7.6312980	2.2737755	1.8932279	1.6469740	1.1667894	0.6388714	0.7526443	0.1662670
ubnfrn	6.2776359	1.6068863	1.4278792	1.2746929	0.9005033	0.5026498	0.5389823	0.1286711
glsmear	5.6436938	1.2945712	1.2099487	1.1003475	0.7757972	0.4388550	0.4389209	0.1110644
target	5.6763000	1.3356000	1.2243000	1.1130000	0.7791000	0.4452000	0.4452000	0.1113000
lbnfrn	5.0097517	0.9822560	0.9920183	0.9260022	0.6510911	0.3750602	0.3388594	0.0934576
lsmltns	3.6560895	0.3153668	0.5266696	0.5537211	0.3848050	0.2388386	0.1251974	0.0558617
sd(mean)	0.1094374	0.0539149	0.0376213	0.0300972	0.0215280	0.0110129	0.0172736	0.0030395
%rsd	1.9279703	4.0367577	3.0728835	2.7041529	2.7631893	2.4736955	3.8799635	2.7308667

Hotelling T^2 Statistic = 1.1519 Critical Value = 329.9 Degrees of Freedom = 13 alpha = 0.001

Pour # 3. Time Pour Occurred After Start of Batch = 99.8 Hours. Duration of Batch = 108.6 Hours.

	SiO_2	Na_2O	Fe_2O_3	B_2O_3	Al_2O_3	K_2O	ThO_2	FsnPrd
dscrm	7.5789273	-32.125	-24.499	33.7068541	19.2543515	-34.312	58.5780831	-176.82
usmltns	7.7302144	2.3163724	1.9217601	1.6673728	1.1845611	0.6462516	0.7666458	0.1685701
ubnfrn	6.2871173	1.6183325	1.4323931	1.2774806	0.9038470	0.5035672	0.5422253	0.1291557
glsmear	5.6112914	1.2914290	1.2032145	1.0948877	0.7723840	0.4367458	0.4371255	0.1106972
target	5.6763000	1.3356000	1.2243000	1.1130000	0.7791000	0.4452000	0.4452000	0.1113000
lbnfrn	4.9354655	0.9645256	0.9740359	0.9122948	0.6409210	0.3699243	0.3320256	0.0922388
lsmltns	3.4923684	0.2664857	0.4846689	0.5224026	0.3602068	0.2272400	0.1076051	0.0528243
sd(mean)	0.1166678	0.0564333	0.0395631	0.0315210	0.0226944	0.0115354	0.0181434	0.0031865
%rsd	2.0553491	4.2253161	3.2314857	2.8320752	2.9129058	2.5910553	4.0753310	2.8629630

Hotelling T^2 Statistic = 0.6267 Critical Value = 329.9 Degrees of Freedom = 13 alpha = 0.001

FIGURE 7.10. Multivariate Control Chart for CFMUT Batch Mean Vectors for the Perturbed Data. Batch-to-batch covariance matrix is not included. (Extremely large initial critical values set equal to 234. First 4 batches are 0.0 because of insufficient data to calculate statistic.)

does not appear to be sensitive to the perturbation. This is because the batch covariance matrix is estimated from the process data, and if the process is not in control the estimate is inflated by portions of the deviations from the process target composition due to the assignable causes. As a result, the batch-to-batch differences are obscured. Methods to counter this difficulty are outlined below.

Table 7.7 gives the usual statistics for the fourteenth CFMUT batch of the perturbed data, although the Bonferroni confidence interval for ThO_2 , batch covariance excluded, does not include the target value. However, for most of the other batches several of the Bonferroni confidence intervals (batch covariance matrix excluded) do not include the target value. Since the batch covariance matrix is estimated from the process data and the

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FIGURE 7.11. Multivariate Control Chart for CFMUT Batch Mean Vectors for the Perturbed Data. Batch-to-batch covariance matrix is included. (Extremely large initial critical values set equal to 234. First 9 batches are 0.0 because of insufficient data to calculate statistic.)

magnitudes of its elements are too large, none of the confidence intervals for which the batch covariance matrix is included detect any deviations from the target compositions.

Note the magnitudes of the elements of the discriminant function for the case when the batch covariance matrix is excluded. They are larger than those observed for the unperturbed data. The deviations of the oxide means from their respective target values are multiplied by the coefficients of the discriminant function. The larger the coefficient, the smaller the deviation that can be detected by the Hotelling T^2 statistic. Note that the second largest coefficient is that of ThO_2 .

Batch 14

Without Batch to Batch Variability

[illegible]

With Batch to Batch Variability

[illegible]

7.3.2 Alternative Estimates of Batch Covariance Matrix for an Out-of-Control Process

When the process goes out of statistical control there are two sources of batch-to-batch variation, the usual random batch fluctuations and fluctuations due to some correctable cause or causes. When the LFCM process is not in control it would not be appropriate to base the statistics of the control charts on the batch covariance matrix estimated from the data. There are two solutions to the problem of deriving an appropriate estimate of the batch covariance matrix of the acceptable random batch-to-batch fluctuations. One solution is to use an estimate of the batch covariance matrix, or some multiple of it, estimated from "good" data obtained from the process when it is in statistical control. The second solution is to use an approximation to the batch covariance matrix until the process is control. Both of these solutions are demonstrated below. The first solution is preferred to the second if "good" data are available.

7.3.2.1 Estimates Based on "Good" Data

If a process is in statistical control, the batch-to-batch differences can be used to estimate the batch covariance matrix. Once the process has operated long enough to obtain data for calculating precise estimates of the batch covariance matrix, control charts for future observations can be based on that estimate. This assumes that the value of the true batch covariance matrix remains constant (this assumption also applies to all other covariance matrices used).

For this demonstration it was assumed that the unperturbed data constitutes the needed historical data from an LFCM process that is in statistical control. The covariance matrices have been estimated from this unperturbed data. It is assumed that this estimate reflects an acceptable amount of batch variation compatible with the operational goals. For example, Figures 7.12 and 7.13 give the process control charts for the perturbed CFMUT data, excluding and including the batch covariance matrix, respectively. The control chart excluding the batch covariance matrix is also given. The covariance matrices used in these charts were estimated from all of the unperturbed CFMUT data.

FIGURE 7.12. Multivariate Control Chart for CFMUT Batch Mean Vectors for the Perturbed Data. Batch-to-batch covariance matrix is not included. (Covariance matrices estimated from all of the CFMUT unperturbed data.)

Note that Figure 7.13 gives a more sensitive control chart than does Figure 7.11. This is because the assignable causes are not included in the estimate of the batch covariance matrix. Since the batch covariance is not updated with each batch, the critical value is constant for all batches.

If Figure 7.13 is not sensitive enough, the sensitivity can be increased by multiplying the estimate of the batch covariance matrix by some appropriate fraction before it is used to calculate the Hotelling T^2 statistics. For example, if the batch covariance matrix had been multiplied by $1/2$, then a similar control chart would have been produced and batches 4, 11, 12, 21, and 23 would have been declared significantly different from the target composition. As Figure 7.13 is now, the LFCM process would not be declared out of control because the fluctuations in the true batch mean vectors do not exceed the random fluctuations due to batches, sampling, and analyses. Care must be used in selecting an appropriate scaling factor for the batch covariance matrix because changing the matrix changes the region of glass

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FIGURE 7.13. Multivariate Control Chart for CFMUT Batch Mean Vectors for the Perturbed Data. Batch-to-batch covariance matrix is included. (Covariance matrices estimated from all of the CFMUT unperturbed data.)

compositions that the control scheme will treat as acceptable. (Increasing the number of samples will also increase the sensitivity of the control scheme, if the magnitudes of the elements of the batch covariance matrix are similar to the magnitudes of the elements of the sampling and analytical covariance matrices).

Table 7.8 gives the statistics for the fourteenth batch of the CFMUT when the covariance matrices are calculated from "good" data. Again, only ThO_2 is shown to deviate from its target for the control scheme that excludes the batch covariance matrix. This, along with the discriminant functions and other like linear combinations of the oxide concentrations, cause the "without batch-to-batch covariance matrix" scheme to deviate from the target composition.

Batch 14								
Without Batch to Batch Variability								
	SiO ₂	Na ₂ O	Fe ₂ O ₃	B ₂ O ₃	Al ₂ O ₃	K ₂ O	ThO ₂	FsnPrd
dscrm	279.143	188.834	-71.295	41.8822397	-187.43	1908.11	-6983	22714.3
usmltns	1.0410798	0.2228755	0.2150410	0.1911805	0.1360473	0.0784249	0.0701449	0.0192400
ubnfrn	0.9863152	0.2162932	0.2038531	0.1857694	0.1294047	0.0765506	0.0661044	0.0186396
mean	0.8554454	0.2005636	0.1771176	0.1728385	0.1135310	0.0720717	0.0564490	0.0172048
target	0.8772000	0.2064000	0.1892000	0.1720000	0.1204000	0.0688000	0.0688000	0.0172000
lbnfrn	0.7245756	0.1848339	0.1503821	0.1599077	0.0976574	0.0675927	0.0467935	0.0157700
lsmltns	0.6698110	0.1782516	0.1391943	0.1544966	0.0910148	0.0657185	0.0427530	0.0151696
sd(mean)	0.0299390	0.0035985	0.0061163	0.0029582	0.0036314	0.0010246	0.0022089	0.0003282
%rsd	3.4130231	1.7434418	3.2326983	1.7198710	3.0161254	1.4893069	3.2105736	1.9083506
Hotelling T ² Statistic = 87.608 Critical Value = 38.45 Degrees of Freedom = 50 alpha = 0.001								
With Batch to Batch Variability								
	SiO ₂	Na ₂ O	Fe ₂ O ₃	B ₂ O ₃	Al ₂ O ₃	K ₂ O	ThO ₂	FsnPrd
dscrm	45.5632596	138.684	-74.128	-785.39	-599.76	1972.52	-1724.4	5120.3
usmltns	1.1073280	0.2746203	0.2377705	0.2153167	0.1469642	0.0886071	0.0832973	0.0226319
ubnfrn	1.0039891	0.2442373	0.2128866	0.1978894	0.1332477	0.0818232	0.0722823	0.0204053
mean	0.8554454	0.2005636	0.1771176	0.1728385	0.1135310	0.0720717	0.0564490	0.0172048
target	0.8772000	0.2064000	0.1892000	0.1720000	0.1204000	0.0688000	0.0688000	0.0172000
lbnfrn	0.7069017	0.1568898	0.1413486	0.1477877	0.0938144	0.0623202	0.0406156	0.0140042
lsmltns	0.6035628	0.1265069	0.1164648	0.1303604	0.0800979	0.0555362	0.0296006	0.0117776
sd(mean)	0.0306955	0.0090249	0.0073914	0.0051766	0.0040743	0.0020151	0.0032719	0.0006614
%rsd	3.4992577	4.3725122	3.9066661	3.0096354	3.3839772	2.9288924	4.7556000	3.8452033
Hotelling T ² Statistic = 30.333 Critical Value = 67.336 Degrees of Freedom = 24 alpha = 0.001								

7.3.2.2 No Available Estimates of the Covariance Matrices

Reasonable estimates of the covariance matrices may be available. If they are not, or if an out-of-statistical-control process is the source of data, then a method for approximating the covariance matrices can be used. There should be no difficulty in estimating the covariance matrices that result from sampling and analyses. However, if an estimate of the batch covariance matrix is needed, the out-of-control data will be the only source for estimation. Estimates of the batch covariance matrix based on this data will produce control charts similar to those in Figure 7.11. Therefore, it is proposed that the matrix estimate based on the out-of-control data be modified.

To approximate the batch covariance matrix, the magnitude of the elements of the batch covariance matrix estimated from the out-of-control data can be altered. If a batch covariance matrix is estimated from the out-of-control data, then a diagonal matrix is formed from the square roots of the main diagonal elements of the estimated batch covariance matrix. The estimated batch covariance matrix is then pre- and post-multiplied by the inverse of this diagonal matrix, resulting in a correlation matrix. This correlation matrix is then pre- and post-multiplied by a new diagonal matrix that has diagonal elements whose square gives the desired magnitude. This is done only to the batch covariance matrix and not to the other covariance matrices.

Since the estimate of the batch covariance matrix is based on out-of-control data, the correlation matrix mentioned above will not be the same as the correlation matrix that would be obtained from a batch covariance matrix based on in-control data. This method ignores the fact that estimated batch correlations are not correct, but merely adjust the magnitude of the variances and covariances. This approximate batch covariance matrix is then used in the control scheme to bring the process into better statistical control. Eventually, the statistical control of the process will permit an in-control estimate of the batch covariance matrix from the new process data.

Figures 7.14 through 7.16 demonstrate this approximation method for three different magnitudes of batch variation. Figures 7.14 through 7.16

FIGURE 7.14. Multivariate Control Chart for CFMUT Batch Mean Vectors for the Perturbed Data. Batch-to-batch covariance matrix is $\text{inv}(\text{Dt}) \cdot \text{Rb} \cdot \text{inv}(\text{Dt})$, where $\text{Dt} = (1/2) \cdot \text{Diag } 0.02 \cdot (\text{target mean vector})$. (Extremely large initial critical values set equal to 234. First 9 batches are 0.0 because of insufficient data to calculate statistic.)

give the "batch covariance matrix included" control chart for which the new diagonal matrix had elements that were 1%, 0.5%, and 0.25% of the target compositions. As the fraction becomes smaller, the sensitivity of the control chart increases. These control charts assume that it is necessary to accumulate the batch data into the estimate of the batch correlation matrix. This will be necessary the first time the system is run or tested.

Figures 7.12 through 7.16 show that it is possible to have a process control scheme that allows an acceptable amount of batch-to-batch variability. If the system is in statistical process control, the sensitivity of the process control scheme can be changed. Also, if the system is out of statistical control, the control scheme that allows some batch-to-batch variation can still be used.

FIGURE 7.15. Multivariate Control Chart for CFMUT Batch Mean Vectors for the Perturbed Data. Batch-to-batch covariance matrix is $\text{inv}(\text{Dt}) \cdot \text{Rb} \cdot \text{inv}(\text{Dt})$, where $\text{Dt} = (1/4) \cdot \text{Diag } 0.02 \cdot (\text{target mean vector})$. (Extremely large initial critical values set equal to 234. First 9 batches are 0.0 because of insufficient data to calculate statistic.)

7.3.3 MFT Control Charts and Example Batch

Figures 7.17, 7.18 and Table 7.9 for the MFT correspond to Figures 7.12, 7.13, and Table 7.8 for the CFMUT. The covariance matrices were estimated from the unperturbed MFT data. The patterns of the Hotelling T^2 statistics are similar to those of the CFMUT. In the simulation, different assignable causes occurred in both the CFMUT and the MFT. However, the effects of the assignable cause in the CFMUT dominate the perturbation in the MFT so that both charts show similar patterns: both oscillate up and down with slight upward trends, and there are no sharp changes in the patterns in the MFT such as steps or changes in the slopes of the patterns. Differences between the control charts for the two tanks are largely due to the remixing of the CFMUT caused by different heel volumes in the MFT. The only notable difference

FIGURE 7.16. Multivariate Control Chart for CFMUT Batch Mean Vectors for the Perturbed Data. Batch-to-batch covariance matrix is $\text{inv}(\text{Dt}) * \text{Rb} * \text{inv}(\text{Dt})$, where $\text{Dt} = (1/8) * \text{Diag } 0.02 * (\text{target mean vector})$. (Extremely large initial critical values set equal to 234. First 9 batches are 0.0 because of insufficient data to calculate statistic.)

between the CFMUT and MFT control charts is that the MFT control chart indicates two batches are out of statistical control.

7.3.4 Transfer of Waste/Frit Slurry from the CFMUT to the MFT

Figure 7.19 is the multivariate process control chart for batch transfers of waste/frit slurry from the CFMUT to the MFT. The sampling and analytical covariance matrices are unaffected by anomalous batch-to-batch differences. Therefore, the sampling and analytical covariance matrices were estimated from the perturbed data. This chart incorporates the correct variance-covariance structure, just as in the case of Figure 7.5. Again, no problems are detected during transfers of waste/frit slurry from the CFMUT to the MFT.

Note that this control chart checks the transfer of waste/frit slurry from the CFMUT to the MFT, even though neither tank is in statistical

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FIGURE 7.17. Multivariate Control Chart for MFT Batch Mean Vectors for the Perturbed Data. Batch-to-batch covariance matrix is not included. (Covariance matrices estimated from all of the MFT unperturbed data.)

control. This scheme works because unbiased estimates of the batch mean vectors in both the CFMUT and MFT, along with unbiased estimates of the true MFT volumes, are used.

Table 7.10 contains the discriminant function coefficients, confidence intervals, differences between CFMUT and MFT batch mean vector estimates, and standard deviations of the differences for the transfer of material for the fourteenth batches of the CFMUT and MFT.

7.3.5 Further Investigations When the Process is Not in Control

The control schemes demonstrated above can be used for two objectives. First, they can be used in the traditional sense where the process is stopped and the assignable causes are identified and corrected. Second, they can be used to flag batches that are out of statistical control but are still

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FIGURE 7.18. Multivariate Control Chart for MFT Batch Mean Vectors for the Perturbed Data. Batch-to-batch covariance matrix is included. (Covariance matrices estimated from all of the MFT unperturbed data.)

acceptable. It is hoped that the inclusion of some batch-to-batch variation into the process control schemes will permit the traditional use of the control schemes.

If these process control schemes are used in the traditional sense and the process goes out of statistical control, the process is stopped and three steps are followed to get the process back on line: the possible causes are identified, the data are gathered to determine the possible causes, and the cause is corrected before the process is restarted.

In the case of the CFMUT perturbed data, there is no reason to stop the process if the random batch variation used in Figure 7.13 is acceptable. If a smaller amount of batch-to-batch variation is acceptable then CFMUT batches would be declared unacceptable, and the process would be stopped after the first batch that is out of statistical control. The composition of the batch can be estimated to determine if any of the oxides deviate significantly from

Batch 14								
Without Batch to Batch Variability								
	SiO ₂	Na ₂ O	Fe ₂ O ₃	B ₂ O ₃	Al ₂ O ₃	K ₂ O	ThO ₂	FsnPrd
dscrm	99.7640812	-2893.5	1805.75	-366.99	-1624.7	-3970.1	-4378.9	-15684
usmltns	1.0055033	0.2108771	0.2212118	0.1834373	0.1390325	0.0732548	0.0736411	0.0184917
ubnfrn	0.9549638	0.2040842	0.2107032	0.1784070	0.1318691	0.0712350	0.0690627	0.0178979
mean	0.8363671	0.1881438	0.1860437	0.1666026	0.1150594	0.0664954	0.0583190	0.0165045
target	0.8772000	0.2064000	0.1892000	0.1720000	0.1204000	0.0688000	0.0688000	0.0172000
lbnfrn	0.7177704	0.1722034	0.1613842	0.1547983	0.0982497	0.0617559	0.0475753	0.0151110
lsmltns	0.6672309	0.1654105	0.1508757	0.1497679	0.0910863	0.0597361	0.0429969	0.0145172
sd(mean)	0.0270287	0.0036329	0.0056200	0.0026903	0.0038310	0.0010802	0.0024485	0.0003176
%rsd	3.0812515	1.7601184	2.9704099	1.5641053	3.1819065	1.5700136	3.5589240	1.8463495
Hotelling T ² Statistic = 119.66 Critical Value = 39.16 Degrees of Freedom = 48 alpha = 0.001								
With Batch to Batch Variability								
	SiO ₂	Na ₂ O	Fe ₂ O ₃	B ₂ O ₃	Al ₂ O ₃	K ₂ O	ThO ₂	FsnPrd
dscrm	-34.852	-501.88	886.073	-142.83	-91.887	609.08	-2922.8	4273.02
usmltns	1.0375081	0.2453481	0.2355967	0.2070088	0.1493582	0.0826592	0.0786457	0.0196962
ubnfrn	0.9527094	0.2212314	0.2147057	0.1899740	0.1348982	0.0758448	0.0700762	0.0183506
mean	0.8363671	0.1881438	0.1860437	0.1666026	0.1150594	0.0664954	0.0583190	0.0165045
target	0.8772000	0.2064000	0.1892000	0.1720000	0.1204000	0.0688000	0.0688000	0.0172000
lbnfrn	0.7200249	0.1550562	0.1573817	0.1432312	0.0952206	0.0571461	0.0465618	0.0146583
lsmltns	0.6352262	0.1309395	0.1364908	0.1261964	0.0807606	0.0503317	0.0379922	0.0133127
sd(mean)	0.0238304	0.0067773	0.0058708	0.0047872	0.0040636	0.0019150	0.0024082	0.0003781
%rsd	2.7166455	3.2835986	3.1029836	2.7832402	3.3750749	2.7834650	3.5003423	2.1985403
Hotelling T ² Statistic = 35.039 Critical Value = 71.24 Degrees of Freedom = 23 alpha = 0.001

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FIGURE 7.19. Multivariate Control Chart for Differences Between MFT Batch Means and MFT Batch Means Predicted from CFMUT Batch Mean Vectors for the Unperturbed Data. (Large critical values set equal to 100. First two batches are 0.0 because of insufficient data to calculate the test statistic.)

their respective target values. Possible causes are then identified, and each of the possible causes is investigated until the specific cause or causes are identified. The process is restarted after the problem has been corrected.

In the case of the MFT, the process would have been stopped on the twentieth batch if Figure 7.18 was used to judge the control of the system. The Bonferroni confidence intervals show that the concentrations of B_2D_3 , K_2O , and fission products are significantly below their target compositions. The aspects of the LFCM that can cause these concentrations to be low are then identified, investigated, and corrected. For this case, the most easily identifiable cause of this out-of-control MFT batch is a problem with the heel volumes in the CFMUT.

TABLE 7.10. Discriminant Function, Simultaneous Confidence Intervals ($\alpha = 0.001$), Bonferroni Confidence Intervals ($\alpha = 0.001/16$), Estimated Batch Means, Target Means, Standard Deviation of the Estimated Batch Means and $\%RSD = 100 \times \text{sd}(\text{mean})/\text{target}$ for the Difference Between the MFT Raw Means and MFT Means Predicted from the CFMUT Means for Batch 14 of the "Perturbed" CFMUT Data. Prefixes "u" and "l" distinguish upper and lower confidence interval limits. For each batch these statistics are calculated with and without including the batch-to-batch variability. Also, the Hotelling T^2 statistic along with its critical value is given.

Batch 14								
	SiO_2	Na_2O	Fe_2O_3	B_2O_3	Al_2O_3	K_2O	ThO_2	FsnPrd
dscrm	-144.56	-324.56	686.632	94.3036743	-60.063	-1755	563.975	-1448.1
usmltns	0.1790193	0.0185404	0.0504622	0.0167020	0.0246130	0.0049999	0.0136694	0.0016858
ubnfrn	0.1279093	0.0110950	0.0393332	0.0113418	0.0185185	0.0026919	0.0101490	0.0011091
diffnrc	-0.0000225	-0.0075412	0.0114763	-0.0020751	0.0032638	-0.0030851	0.0013374	-0.0003344
lbnfrn	-0.1279543	-0.0261775	-0.0163806	-0.0154920	-0.0119909	-0.0088621	-0.0074743	-0.0017779
lsmltns	-0.1790643	-0.0336228	-0.0275097	-0.0208522	-0.0180854	-0.0111701	-0.0109946	-0.0023546
sd(diff)	0.0295521	0.0043049	0.0064349	0.0030993	0.0035238	0.0013345	0.0020355	0.0003334
Hotelling T^2 Statistic = 16.592 Critical Value = 36.706 Dgrees of Freedom = 56 $\alpha = 0.001$								

7.4 IMPACT OF PERTURBATIONS

The variability of the true glass composition that resulted from the simulation of the perturbed process is depicted for two components, silicon and sodium, in Figure 7.20. No effect of the bias in measurement of volume in the CFMUT at 600 hours is apparent, and no effect was detected using statistical process control. The introduction of the precipitation/resuspension process in the MFT at 1200 hours is apparent in the figure, but the resulting variability in the glass is small. The silica composition varies within 0.005 of the target value of 0.51 before 1200 hours, and within 0.01 of the 0.51 target value after 1200 hours, with a negative shift in the mean of about 0.005. The effect on the sodium composition is qualitatively similar, except the mean increased slightly.

The change apparent at 1200 hours when examining the true glass composition is not available to the plant operator, who can only observe measured

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FIGURE 7.20. Increasing Bias in CFMUT Volume After 1200 Hours

compositions. However, the process would have been declared out of statistical control at about 2050 hours, based on the MFT control chart as discussed in section 7.3.5. Hence, in this case, the departures from ideality introduced into the simulation were barely detectable, but caused only small changes in the composition of the glass.

8.0 MULTIVARIATE STATISTICAL ANALYSIS OF CHEMICAL DURABILITY OF WASTE GLASSES

In controlling the process it is desirable to limit the number of variables whose values are to be constrained. In the case of a waste vitrification system, one important quality characteristic of the glass to be achieved is adequate chemical durability. Plodinec, Jantzen, and Wicks (1984) and Grambow (1985) have related the durability of nuclear waste glasses to their composition by calculating a free energy of hydration for each glass and correlating it with the chemical durabilities.

It is also possible to reduce such data using purely statistical methods. Data accumulated by Plodinec, Jantzen, and Wicks^(a) and by Chick et al. (1984) were analyzed to examine the relationship between the logarithm of chemical durability and the composition of the glass. The release of boron into solution after 28 days in a static leach test was taken to be the measure of chemical durability.

The data were analyzed using the "partial least squares" (PLS) method (Wold 1982). This is an extension of the principal components method for extracting from a covariance matrix a set of variables that are each linear combinations of the original variables used to form the matrix. These new variables, called principal components, more clearly reveal the source of the covariances. Often the majority of the variance over the independent variables is explained by a few principal components; if so, it implies that some of the supposedly independent variables are in fact not statistically independent, and should be reduced to a fewer number of variables (viz., principal components) before attempting correlations with a dependent variable.

The PLS method differs from the principal components method in that the principal components are "rotated" (thinking of the principal component in a vector in "space" where the "directions" are the different independent variables, e.g., weight fractions) to line up better with a "vector"

(a) We are indebted to Dr. Carol Jantzen of Savannah River Laboratory for making these data available.

representing the dependent variable, e.g., chemical durability. This forms a clearer picture of the contribution of the independent variables in predicting the values of the dependent variable. Specifically, the relative importance of the independent variables in predicting the dependent variable is established.

When applied to correlating the chemical durability of a collection of nuclear waste glasses to the composition of the glasses, the PLS method reveals the relative importance of different chemical elements to the correlation. The importance is revealed by examining the contribution of the weight fractions of the elements to the PLS components. These contributions are termed "loadings," and describe how a PLS component is formed as a linear combination of the weight fractions. The magnitude of the loadings is not easily interpreted, but the relative magnitudes of the loadings describe the relative importance of the weight fractions to the chemical durability.

The result of applying a PLS analysis to the data of Plodinec, Jantzen, and Wicks and of Chick et al. (1984) is as follows.

<u>Element</u>	<u>First PLS Comp.</u>	<u>Second PLS Comp.</u>	<u>Third PLS Comp.</u>
Al	-0.32	-0.24	-0.08
Ca	-0.06	0.34	-0.14
Fe	-0.02	-0.15	-0.45
Mg	-0.11	0.41	0.34
Mn	-0.10	0.19	-0.39
Na	0.53	0.04	0.06
Li	-0.03	0.37	-0.08
Ni	-0.06	0.06	-0.28
Si	-0.48	-0.17	0.08
Cr	0.13	-0.30	0.21
B	0.49	0.11	-0.08
Sr	0.06	-0.19	0.35
Zr	-0.08	0.05	0.27
Ti	-0.20	0.31	0.22
K	-0.14	0.26	0.10
Cs	-0.04	-0.20	0.14
P	0.15	-0.28	0.24
Nd	-0.08	-0.10	0.18

For the data examined, the " R^2 " value is 0.75, meaning that 75% of the variance of the dependent variable (chemical durability) can be explained by

the non-random effect of the independent variables (weight fractions). Practically all of this variance is explained by only the first three of the PLS components. These components are as shown above; the values in the columns are the "loadings" that show how each of the three components depend linearly on the weight fractions of the chemical elements listed.

The first PLS component alone explains about 50% of the variance. A component constructed instead by "loading" in proportion to the free energies of hydration of the chemical elements, which is equivalent to applying the free energy of hydration correlation discussed above, explains about 40% of the variance. From a purely statistical point of view, the first PLS component does as well or better than the free energy of hydration in explaining the data. Therefore, it is worth examining the loadings to see what is implied.

The first PLS component depends most strongly on the aluminum, sodium, silicon, and boron weight fractions. The signs of the loadings show that, to a rough first approximation, the chemical durability depends on the ratio of the weight fractions of sodium and boron to silicon and aluminum. This implies that in trying to control a waste vitrification process to maintain acceptable chemical durability of the glass, emphasis should be put on controlling the ratio (for example) of sodium and boron to silicon and aluminum. This implication needs further confirmation, but if confirmed suggests that the fluctuation of some chemical components during processing may need to be closely controlled, while others may not be important enough to be included in process control criteria. For example, given the above results it might be desirable to independently control the sodium, boron, silicon, and aluminum weight fractions when adding chemicals to form the melter feed from the waste, while also being unnecessary to control other chemical species.

9.0 CONCLUSIONS

1. With respect to waste form qualification, a practical definition of a successful system for monitoring and controlling an inherently fluctuating waste vitrification process is the ability to detect departures from assumed ideal process behavior that are great enough to substantially affect the quality of the product. For example, if it is proposed that a specified fraction of all glass produced falls in a range of compositions that provides a specified maximum leach rate, then glass falling outside this range of compositions could be taken as a definition of substantially affecting the quality of the glass.
2. The fluctuating behavior of compositions in a waste vitrification process can be simulated in terms of a set of cases, each consisting of a set of tests to be satisfied and a set of actions to then be taken. The tests should include at least: tank volume, stream flow, and conditions signified by true/false flags. The actions should include at least: setting a flag, setting a flag after a specified delay, turning a stream on or off, evaporation, sampling tank contents, chemical addition, testing tank contents, and resetting tank masses to zero.
3. Mass balances and separation of mass in a process can be simulated sufficiently to address waste form qualification issues by considering the distribution of chemical components among phases upon entering a tank, and in terms of the relative access of the phases to a stream exiting the tank.
4. Multivariate statistical methods for analysis of variance and covariance can be combined with simplified mass balance equations cast in matrix form to estimate compositions and their variance-covariance matrix for a vitrification process, where information from different tanks and different times is used simultaneously.
5. The variance-covariance matrix for compositions can be combined into a single statistic approximately distributed as "Hotelling's T^2 " statistic

to provide a reduced variable for process control charting. This will be sensitive simultaneously to composition data over all components, tanks, and previous sample times.

6. The introduction of a hypothetical precipitation/resuspension process in the melter feed tank in a simulated vitrification process caused a small shift in the silica composition of the glass produced. The perturbation was detected from simulated process data by process control charting, but not until after 800 hours. We conclude that this particular hypothetical perturbation was difficult to detect but did not significantly affect the quality of the glass.
7. Given a preliminary multivariate statistical analysis of glass leach data, it might be desirable to emphasize control of the sodium, boron, silicon, and aluminum weight fractions when adding chemicals to form the melter feed from the waste. However, this takes into consideration only the chemical durability of the glass.

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APPENDIX A

ANNOTATED CASE INPUT FILE FOR CONTROL OF PROCESS SIMILAR TO WVOP PROCESS

APPENDIX A

ANNOTATED CASE INPUT FILE FOR CONTROL OF PROCESS SIMILAR TO WVDP PROCESS

<u>ENTRIES IN INPUT FILE</u>	<u>ANNOTATION</u>
CASE: WASTE TANK EMPTY	
VOLUME	Is there no more waste?
WASTE TANK EMPTY	[Has measured volume decreased
WASTE	to zero?]
F	
0.	
END TESTS	
STREAM	Stop trying to pump waste to CFMUT
STOP WASTE TO CFMUT	
WASTE TO CFMUT	
F	
SET FLAG	Signify to rest of simulation that
WASTE AVAILABLE	waste is gone
F	
END ACTIONS	
CASE: ACCEPT SBS DRAIN	
CONDITION	Is there need to drain SBS?
SBS DRAIN REQUESTED	
T	
CONDITION	And, is CFMUT ready to receive liquid?
CFMUT READY FOR FILL	
T	
END TESTS	
STREAM	Start transfer from SBS
SBS DRAIN ON	
SBS TO CFMUT	
T	
SET FLAG	Now OK to send condensate to SBS
OFFGAS ALLOWED	
T	
END ACTIONS	
CASE: SBS DRAIN REQUESTED	

VOLUME
SBS HIGH ENOUGH TO DRAIN
SBS
T
1600.
CONDITION
SBS DRAIN REQUESTED
F
END TESTS

Check SBS level to see if OK to drain
[Has measured volume increased
to 1600 gallons?]

This flag checked so action is not asked
to repeat itself due to random
fluctuations in measurement of SBS volume

SET FLAG
SBS DRAIN REQUESTED
T
END ACTIONS

Set flag for use in other cases

CASE: STOP SBS DRAIN

VOLUME
SBS DOWN TO LOW LEVEL
SBS
F
800.
STREAM
SBS TO CFMUT
T
END TESTS

Check to see if SBS drain is complete
[has measured volume decreased
to 800 gallons?]

Requires this stream to be "on" before
trying to turn it off

STREAM
STOP SBS DRAIN
SBS TO CFMUT
F
SET FLAG
SBS DRAIN REQUESTED
F
END ACTIONS

Turn off drain stream

No longer requesting to drain SBS

CASE: SBS TOO HIGH

VOLUME
SBS ABOVE HIGH LIMIT
SBS
T
5000.
STREAM
SBS TO CFMUT
F
END TESTS

SBS must be drained before accepting
any more condensate
[Has measured volume increased
to 5000 gallons?]

Is there a need to turn stream off?

SET FLAG

Signify request to other cases

SBS DRAIN REQUESTED

T

SET FLAG

OFFGAS ALLOWED

F

SET FLAG

FEEDING ALLOWED

F

STREAM

INTERRUPT MELTER FEED

MFT TO MELTER

F

END ACTIONS

Signify cannot continue to vaporize water
in melter

Signify that feeding must be stopped

Stop feeding melter

CASE: FILL CFMUT

CONDITION

WASTE AVAILABLE

T

CONDITION

CFMUT READY FOR FILL

T

CONDITION

SBS DRAIN REQUESTED

F

END TESTS

Is there waste to send to CFMUT?

Is the CFMUT ready to accept waste?

Is draining not complete?

STREAM

START FILLING CFMUT

WASTE TO CFMUT

T

SET FLAG

CFMUT READY FOR FILL

F

SET FLAG

CFMUT SAMPLE AVAILABLE

F

END ACTIONS

Send waste to CFMUT

No longer ready to start filling

New waste in CFMUT not yet sampled

CASE: START CFMUT CONCENTRATION

VOLUME

CFMUT AT FILL LEVEL

CFMUT

T

5000.

STREAM

WASTE TO CFMUT

T

Has the CFMUT been filled?
[Has measured volume increased
to 5000 gallons?]

Is transfer still in progress?

END TESTS

STREAM
STOP CFMUT FILL
WASTE TO CFMUT
F
SAMPLE
SAMPLE WASTE IN CFMUT
CFMUT
3
3
.02
BATCH REPORT
CFMUT WASTE
SAMPLE WASTE IN CFMUT
T
DELAY
START CFMUT SAMPLE DELAY
OUT OF CFMUT SAMPLE DELAY
24.
EVAPORATE
EVAPORATE CFMUT
SAMPLE WASTE IN CFMUT
CFMUT EVAPORATION
CFMUT AT FILL LEVEL
CFMUT AT CONCENTRATION LEVEL
0.35
END ACTIONS

Stop sending waste to CFMUT

Sample the waste; results will be used
to compute amount of evaporation wanted
and masses of chemicals to add

3 samples, 3 analyses in each
2% sampling error

Record contents of CFMUT

24 hours before sample results can
be acted on

Start evaporating by removing water
through condensate stream

[see text for meaning of entries]

CASE: STOP CFMUT CONCENTRATION
VOLUME
CFMUT AT CONCENTRATION LEVEL
CFMUT
F
2500.
STREAM
CFMUT EVAPORATION
T
END TESTS

CFMUT has reached desired concentration
[Has measured volume decreased to computed
level? Note: value computed by "EVAPORATE"
is actually used--2500 is a dummy value.]

Is condensation in progress?

STREAM
STOP CFMUT CONCENTRATION
CFMUT EVAPORATION
F
END ACTIONS

Turn off condensate stream

CASE: CFMUT READY FOR CHEMADJUST

STREAM

Is condensation complete?

CFMUT EVAPORATION

F

CONDITION

OUT OF CFMUT SAMPLE DELAY

T

END TESTS

Are results of sample available yet?

BATCH REPORT

CFMUT WASTE

SAMPLE WASTE IN CFMUT

F

SAMPLE CFMUT FEED

F

SET FLAG

CFMUT READY FOR CHEMADJUST

T

END ACTIONS

Record final volume of CFMUT batch

Signify ready for computing addition of chemicals

CASE: CFMUT CHEMADJUST

STREAM

CFMUT EVAPORATION

F

CONDITION

CFMUT CHEMADJUST COMPUTED

F

CONDITION

CFMUT READY FOR CHEMADJUST

T

END TESTS

Is condensation complete?

Chem adjust already computed?

Is information available to compute?

CHEMADD

CFMUT CHEMADD

SAMPLE WASTE IN CFMUT

2500.

5000.

0.30

CFMUT VOL ADJUST NEEDED

SET FLAG

CFMUT CHEMADJUST COMPUTED

T

END ACTIONS

Compute addition of chemicals, set flag indicating if could proceed CFMUT

[See text for meaning of entries]

CASE: START CFMUT VOLUME ADJUST

CONDITION

CFMUT CHEMADJUST COMPUTED

T

CONDITION

Has computation been made?

Did computation require reducing

CFMUT VOL ADJUST NEEDED	amount of waste to add chemicals to?
T	
END TESTS	
STREAM	Start draining some of waste from CFMUT
ADJUST CFMUT VOLUME	
CFMUT TO WASTE	
T	
SET FLAG	Now no longer need to drain waste
CFMUT VOL ADJUST NEEDED	
F	
SET FLAG	Will have to recompute chemical addition
CFMUT CHEMADJUST COMPUTED	
F	
SET FLAG	Not ready to compute addition yet
CFMUT READY FOR CHEMADJUST	
F	
DELAY	Control amount drained by timing it
DRAIN CFMUT FOR 1/12 HOUR	
CFMUT ADJUST COMPLETE	Name of flag to be set when time is up
.0833333333	
END ACTIONS	

CASE: STOP CFMUT VOLUME ADJUST

CONDITION	Check to see if delay time is complete
CFMUT ADJUST COMPLETE	
T	
STREAM	Is stream still on?
CFMUT TO WASTE	
T	
END TESTS	

STREAM	Stop draining CFMUT
STOP CFMUT VOLUME ADJUST	
CFMUT TO WASTE	
F	
SET FLAG	Signify to other cases that need to
CFMUT READY FOR CHEMADJUST	compute chemical addition
T	
END ACTIONS	

CASE: START CFMUT-MFT TRANSFER

CONDITION	Chemical addition was computed?
CFMUT CHEMADJUST COMPUTED	
T	
CONDITION	The addition actually occurred?
CFMUT VOL ADJUST NEEDED	

F
CONDITION
MFT READY FOR FILL
T
STREAM
CFMUT TO MFT
F
END TESTS

MFT ready to accept more liquid?

Transfer not already in progress?

BATCH REPORT
CFMUT BATCH
SAMPLE CFMUT FEED
T
STREAM
START CFMUT-MFT TRANSFER
CFMUT TO MFT

Record contents of CFMUT

Send feed to MFT

T
SET FLAG
MFT READY FOR FILL
F
SET FLAG
CFMUT CHEMADJUST COMPUTED
F
SET FLAG
CFMUT READY FOR CHEMADJUST
F
SET FLAG
MFT CONTENTS ACCEPTED
F
END ACTIONS

MFT no longer ready for transfer

Signify will have to recompute
when next batch of waste goes to CFMUT

Signify will have to redetermine when
next batch is ready for computation

Signify will have to redetermine
acceptability of MFT batch

CASE: END OF MFT BATCH

CONDITION
FIRST MFT BATCH
F
STREAM
CFMUT TO MFT
T
END TESTS

Is this not the first MFT batch of the
simulation?

Has transfer to MFT just begun?

BATCH REPORT
MFT FEED AVAILABLE
SAMPLE MFT
F
END ACTIONS

Record final volume in MFT

CASE: CFMUT REACHED HEEL

VOLUME	Have CFMUT contents been transferred?
CFMUT AT TRANSFER LOW LEVEL	[Has measured volume decreased
CFMUT	to 800 gallons?]
F	
800.	
STREAM	Is transfer still occurring?
CFMUT TO MFT	
T	
END TESTS	
STREAM	Turn off transfer stream
STOP CFMUT TO MFT TRANSFER	
CFMUT TO MFT	
F	
SET FLAG	Signify that CFMUT can be refilled
CFMUT READY FOR FILL	
T	
SET FLAG	Signify that have feed for melter
FEED AVAILABLE	
T	
SET FLAG	Signify that ready to take MFT sample
MFT READY FOR SAMPLE	
T	
BATCH REPORT	Record final volume in CFMUT
CFMUT BATCH	
SAMPLE CFMUT FEED	
F	
END ACTIONS	
CASE: MFT READY FOR FILL	
VOLUME	Has MFT been emptied sufficiently to
MFT DOWN TO FILL REQUEST LEVEL	be refilled?
MFT	[Has measured volume decreased
F	to 1000 gallons?]
1000.	
STREAM	Is transfer not already in progress?
CFMUT TO MFT	
F	
CONDITION	Has MFT not been readied for fill?
MFT READY FOR FILL	
F	
END TESTS	
SET FLAG	
MFT READY FOR FILL	
T	Signify MFT ready for filling
END ACTIONS	

CASE: MFT REACHED FILL LIMIT

VOLUME
MFT REACHED FILL LIMIT
MFT
T
5000.
STREAM
CFMUT TO MFT
T
END TESTS

Is MFT filled to limit?
[Has measured volume increased
to 5000 gallons?]

Is filling operation in progress?

STREAM
STOP MFT FILL
CFMUT TO MFT
F
BATCH REPORT
CFMUT BATCH
SAMPLE CFMUT FEED
F
SET FLAG
FEED AVAILABLE
T
SET FLAG
MFT READY FOR SAMPLE
T
SET FLAG
CFMUT READY FOR FILL
T
END ACTIONS

Stop filling MFT

Record final volume in MFT

Signify that have feed for the melter

Signify that ready to take MFT sample

Signify that CFMUT can be refilled

CASE: SAMPLE MFT

CONDITION
MFT READY FOR SAMPLE
T
END TESTS

Is MFT ready to be sampled?

SAMPLE
SAMPLE MFT
MFT
3
3
.02
BATCH REPORT
MFT FEED AVAILABLE
SAMPLE MFT
T
SET FLAG
FIRST MFT BATCH

Sample the contents of the MFT

Record the contents of the MFT

No longer first MFT batch

F
DELAY
MFT SAMPLE BEING ANALYZED
OUT OF MFT SAMPLE DELAY
24.
SET FLAG
MFT READY FOR SAMPLE
F
END ACTIONS

24 hours turnaround time before
sample results are available

No need to sample MFT until refilled

CASE: TEST MFT CONTENTS

CONDITION
OUT OF MFT SAMPLE DELAY
T
END TESTS

Are MFT sample results available?

TEST CONTENTS
TEST MFT CONTENTS
SAMPLE MFT
MFT CONTENTS ACCEPTABLE
0.2
SET FLAG
MFT TESTED
T
END ACTIONS

Check to see if contents of MFT are
acceptable

Signify that contents have been tested

CASE: REJECT MFT CONTENTS

CONDITION
MFT TESTED
T
CONDITION
MFT CONTENTS ACCEPTABLE
F
END TESTS

Have contents of MFT been tested?

Was the test unsuccessful?

SET FLAG
MFT TESTED
F
STREAM
STOP FEEDING MELTER
MFT TO MELTER
F
STREAM
DRAIN MFT TO WASTE
MFT TO WASTE
T
SET FLAG

Will need to retest contents

Contents no good; stop sending
it to melter

Drain MFT contents to waste tank

Feed no longer available for melter

FEED AVAILABLE

F

SET FLAG

FEEDING ALLOWED

F

BATCH REPORT

MFT FEED AVAILABLE

SAMPLE MFT

F

END ACTIONS

Disallow feeding melter

Record volume in MFT when feeding stopped

CASE: STOP MFT REJECT CYCLE

VOLUME

MFT DOWN TO REJECT HEEL

MFT

F

800.

STREAM

MFT TO WASTE

T

END TESTS

Has MFT been drained?

[Has measured volume decreased
to 800 gallons?]

Is draining still in progress?

STREAM

STOP MFT DRAIN TO WASTE

MFT TO WASTE

F

SET FLAG

MFT READY FOR FILL

T

END ACTIONS

Stop draining MFT to waste tank

MFT can be refilled now

CASE: MFT TOO LOW TO FEED

VOLUME

MFT TOO LOW FOR FEEDING

MFT

F

800.

STREAM

MFT TO MELTER

T

END TESTS

Has MFT been emptied by feeding?

[Has measured volume decreased
to 800 gallons?]

Is feeding in progress?

STREAM

STOP FEED TO MELTER

MFT TO MELTER

F

SET FLAG

Stop feeding melter

Signify that feed no longer available

FEED AVAILABLE
F
SET FLAG
FEEDING ALLOWED
F
END ACTIONS

Signify that can no longer feed melter

CASE: START MFT-MELTER FEED

CONDITION
FEEDING ALLOWED
T
END TESTS

Is feeding allowed?

STREAM
START FEED TO MELTER
MFT TO MELTER
T
END ACTIONS

Begin feeding melter

CASE: INTERRUPT MELTER FEED

CONDITION
FEEDING ALLOWED
F
END TESTS

Has feeding been disallowed?

STREAM
INTERRUPT FEEDING
MFT TO MELTER
F
END ACTIONS

Stop feeding melter (until restarted)

CASE: FEEDING ALLOWED

CONDITION
MELTING ALLOWED
T
CONOITION
OFFGAS ALLOWED
T
CONDITION
FEED AVAILABLE
T
END TESTS

Is adding to volume in melter allowed?

And, can condensate be sent to SBS?

And, is feed available to be sent
to melter?

SET FLAG
FEEDING ALLOWED

Then start/resume feeding melter

T
END ACTIONS

CASE: GLASS ABOVE OVERFLOW

VOLUME
ABOVE ZERO OVERFLOW VOLUME
GLASS
T
138.1
STREAM
GLASS OVERFLOW
F
END TESTS

Has the glass reached the point of
overflow?
[Has glass volume increased to 138.1 gal?]
[volume defined to create stable control]

Is overflow not already occurring?

STREAM
GLASS CAN OVERFLOW
GLASS OVERFLOW
T
END ACTIONS

Define that glass is now overflowing

CASE: GLASS BELOW OVERFLOW

VOLUME
BELOW ZERO OVERFLOW VOLUME
GLASS
F
138.
STREAM
GLASS OVERFLOW
T
END TESTS

Has glass volume decreased sufficiently
to define that no longer overflowing?
[Has volume decreased to 138 gallons]

Is overflow occurring?

STREAM
GLASS CANNOT OVERFLOW
GLASS OVERFLOW
F
END ACTIONS

Define that glass is not overflowing

CASE: MELTING NOT ALLOWED

CONDITION
CANISTER IN PLACE
F
CONDITION
GLASS OVERFLOW SAFE
F
END TESTS

Is there no canister to catch pouring
glass?

And, is the glass level no longer low
enough that it is not nearly overflowing?

SET FLAG
 MELTING ALLOWED
 F
 SET FLAG
 FEEDING ALLOWED
 F
 END ACTIONS

Disallow adding to volume of glass

Disallow sending feed to melter

CASE: START GLASS AIRLIFT

VOLUME
 CANISTER AT AIRLIFT LEVEL
 CANISTER
 T
 130.
 STREAM
 GLASS AIRLIFT
 F
 CONDITION
 CHANGE CANISTER
 F
 END TESTS

Is there enough glass in canister
 to top it off by airlifting
 10 gallons of glass into it?

Is airlift not already running?

Need to change canister not signified
 yet?

SET FLAG
 CHANGE CANISTER
 T
 STREAM
 START GLASS AIRLIFT
 GLASS AIRLIFT
 T

Signify that need to change canister

Turn on the airlift

DELAY
 AIRLIFT 200 GPH * 1/20 HR OF GLASS
 AIRLIFT COMPLETE
 .05

Time the operation to transfer 10 gallons

SET FLAG
 GLASS OVERFLOW SAFE
 T
 SET FLAG
 MELTING ALLOWED
 T
 END ACTIONS

Glass level has been decreased, so
 no danger of overflow

Can add to glass volume now

CASE: AIRLIFT COMPLETE

CONDITION
 AIRLIFT COMPLETE
 T
 END TESTS

The timed operation is over

STREAM	Turn off airlift
END GLASS AIRLIFT	
GLASS AIRLIFT	
F	
SAMPLE	Sample contents of melter as last
SAMPLE LAST MELTER GLASS	glass is delivered to canister
GLASS	
1	
3	
0.	
DELAY	2 hours allotted to changing canister
CHANGE OUT CANISTER	
CANISTER IN PLACE	
2.	
RESET TANK	New canister, contains no glass; tank
NEW CANISTER IS EMPTY	masses suddenly set to zero
CANISTER	
BATCH REPORT	Record contents of melter as last
GLASS AT TOP OF CANISTER	glass is delivered to canister
SAMPLE LAST MELTER GLASS	
T	
END ACTIONS	
CASE: GLASS LEVEL NO LONGER SAFE	
VOLUME	Could glass overflow?
GLASS ABOVE SAFE LEVEL	[Has measured volume in melter increased
GLASS	to 132 gallons?]
T	
132.	
END TESTS	
SET FLAG	Signify that not safe from possible
GLASS OVERFLOW SAFE	overflow of glass
F	
END ACTIONS	
CASE: NEW CANISTER	
CONDITION	Is two-hour delay to replace
CANISTER IN PLACE	canister completed?
T	
END TESTS	
BATCH REPORT	Record volume of glass in melter.
GLASS AT TOP OF CANISTER	
SAMPLE LAST MELTER GLASS	
F	
SET FLAG	No longer need to change canister

CHANGE CANISTER
F
SET FLAG
MELTING ALLOWED
T
END ACTIONS

Now have canister to overflow into

END CASES

** End of case file **

APPENDIX B

DESCRIPTION OF METHODS FOR MULTIVARIATE STATISTICAL ANALYSIS OF PROCESS DATA

APPENDIX B

OBJECTIVE

The object of the work summarized in this appendix is to model part of the liquid fed ceramic melter system and use those models to develop methods for estimating the oxide concentrations in the glass and methods for constructing statistical process control schemes to control glass composition to be close to the target composition. Additionally, it was desired that these methods consider all relevant oxides simultaneously and account for the correlations known to exist in such data. Control schemes for controlling uncertainty as opposed to shifts in average composition, are not discussed herein.

The results given in this appendix constitute the theoretical answer to the above objective. Since no real data from the operation of a liquid fed ceramic melter is available, the system is modeled in terms of variables and parameters that will be measured. Multivariate statistical methods are used to develop estimation and process control schemes. When actual or simulated data is made available, it can be analyzed using the methods described herein. Although the results reported here are complex, it is expected that some of the methods will simplify. This does not mean that the results presented here are deliberately complex. On the contrary, the results given here have been made as simple as possible for the expected properties of the data from a liquid fed ceramic melter. The methods may simplify after actual or simulated data are examined because all of the properties provided for in these results may not turn out to be very important and can be ignored. Therefore, the results given here are exact theoretical solutions based on classical statistical methods. They account for all the properties expected in the data.

The results of this report are limited to describing the frit/waste slurry compositions in the frit preparation tank, the melter feed tank and the melter. Process control schemes for monitoring the uncertainties due to process operation and data collection have not been included because of time limitations. Nevertheless, these types of control schemes will also be

necessary to the overall monitoring of a liquid-fed ceramic melter system. Through out this report it is assumed that the tanks and melter are well mixed tanks, and that the slurry composition of each batch remains constant; i.e., material loss through the off-gas system has not been modeled and therefore is implicitly assumed to be zero. Also, the cold-cap in the melter is assumed to have constant volume.

B.1.1 Liquid Fed Ceramic Melter System

The portion of the liquid fed ceramic melter (LFCM) system discussed in this appendix includes the tanks where the frit is mixed with the waste and then fed to the ceramic melter. The waste is batch fed into the frit preparation tank (FPT); it is sampled to determine its composition and then concentrated. From the predicted waste composition, a frit is made and added to the concentrated waste. The frit/waste slurry is then batch fed to the melter feed tank (MFT). From the MFT the frit/waste slurry is continuously fed into the ceramic melter.

The transfer of slurry from the FPT to the MFT and from the MFT to the melter does not completely empty the FPT and MFT. A heel of slurry is always left behind. This heel is assumed to be about 14% of the volume of a batch of slurry. It is assumed that the slurry fed to the ceramic melter becomes part of the cold cap and then enters the glass as material melts off the bottom of the cold cap into the liquid glass. From the melter the glass is poured into steel canisters.

Sampling of the frit/waste slurry occurs in the FPT and MFT. Sampling of the glass occurs after the glass leaves the melter: samples can be taken from either the pour stream or glass shards at the top of a canister. These samples will be used to estimate and monitor the oxide concentrations in the two tanks and melter.

B.1.2 Multivariate Approach

As discussed in a letter report^(a) to the Hanford Waste Vitrification Project (HWVP), concentration information from the FPT and MFT samples can be combined with actual glass sample estimates to obtain a better estimate of the glass composition. It is proposed that multivariate statistical methods be used to 1) monitor the LFCM process and 2) estimate the oxide concentrations in the glass exiting the melter. Multivariate methods are necessary because the oxide concentrations determined from the different tanks are expected to be correlated. Also, batches of frit/waste slurry will be correlated with each other.

The correlations referred to here are linear relationships between the random fluctuations that arise from operating the LFCM, sampling the frit/waste slurry and analyzing the samples. To clarify this, consider analyses made of the concentrations of two oxides:

$$y_i = \mu + \epsilon_i$$

and

$$x_i = \eta + \delta_i \tag{B.1.1}$$

where μ and η are the true concentrations and ϵ_i and δ_i are random errors due to the process, sampling, and making measurements. Researchers are interested in the values and properties of μ and η , but they observe x_i and y_i , where the subscript denotes the i^{th} time the data were taken. The properties of ϵ_i and δ_i determine what the researchers can conclude about μ and η . If x_i and y_i are correlated then the following relationship exists between ϵ_i and δ_i

$$\epsilon_i = a + b \delta_i + w_i \tag{B.1.2}$$

(a) Pulsipher, B. A., et al. June 1987. "Waste Form Qualification Sampling and Analysis Requirements." Work Done in Support of Hanford Waste Vitrification Project by Pacific Northwest Laboratory, Richland, Washington.

where w_i is the part of ϵ_i not accounted for by $a + b \delta_i$. Since ϵ_i and δ_i are related, they carry information about each other and hence estimates of μ and η based on y_i and x_i will contain information about each other. This means that the conclusions based on the estimate of μ are conditional on the conclusions based on the estimate of η and vice versa.

Failure to account for correlation in data from the LFCM will have two effects. First, estimates of oxide concentrations will not have minimum uncertainty. Accounting for correlations permits one to obtain more precise estimates of the true oxide concentrations. Second, if correlations are ignored when constructing process control charts, the charts will fail to detect anomalous concentrations that multivariate process control charts will detect. Both of these effects are illustrated in Figure B.1.

The three types of joint confidence regions illustrated in Figure B.1 are explained as follows. Consider the data represented by (B.1.1). The square region results from constructing a confidence interval for μ and η and declaring any point outside one of the confidence intervals as out of control. This results from considering the variables one at a time ignoring all others. The circle results from constructing a joint confidence region using

FIGURE B.1. Three Types of Confidence Regions for Two Correlated Variables

using a multivariate approach but assuming the correlation is zero. The elliptical region results from multivariate methods accounting for the nonzero correlation. It is assumed for the purposes of this illustration that the ellipse is the correct confidence region.

Conclusions about the values of μ and η based on the elliptical region will be more precise. The three different confidence regions illustrated in Figure B.1 represent three different sets of pairs of values for μ and η . Since the area of the ellipse is smaller than the area of the circle or square, it denotes a set of paired values for μ and η with fewer paired values than either of the other two sets. In this sense, the elliptical region can be said to be a more precise statement about μ and η .

Second, note the points labeled A, B, C, D, and E in Figure B.1. Point 'A' is an oxide pair that is declared out of control by all three confidence regions. Point 'B' is an out of control point detected by the circular and elliptical regions but not the square region. Point 'C' is an out of control point detectable by the square and elliptical regions but not the circular region. Point 'D' is an out of control point detectable only by the elliptical region. Point 'E' is an acceptable oxide concentration pair declared unacceptable by the circular and square confidence regions. Thus, this illustrates that fewer process control errors will be made if process control schemes account for correlations.

B.1.3 Variance and Covariance

Before describing the estimation and control charts developed for the LFCM, two statistical quantities, the variance and the covariance, need to be defined.

Uncertainty in data is usually expressed in terms of standard deviations. For functions of correlated measurements, the standard deviations are square roots of linear combinations of variances and covariances. Hence, to estimate standard deviations of functions of correlated measurements, variances and covariances must be estimated.

The standard deviation is a measure of average spread among data points and is in the same units as the data. The standard deviation is defined

mathematically as the square root of the variance. The variance is in squared units. Variances are mathematically convenient because they are additive whereas standard deviations are not. For example, the variance of the sum of uncorrelated measurements is equal to the sum of the variances of the respective measurements. This is not true for standard deviations as the standard deviation of the above mentioned sum is the square root of the sum of the variances. Geometrically, the variance is the average squared Euclidian distance between the individual measurements and their mean. The standard deviation is therefore, the average Euclidian distance between the data points and their mean.

The correlation between two measurements is determined by calculating the Pearson product moment correlation coefficient, ρ . This coefficient is defined by dividing the covariance between the two measurements by their respective standard deviations:

$$\rho = \frac{\text{Cov}(x,y)}{\sigma_x \sigma_y} \quad (\text{B.1.3})$$

where σ_x and σ_y are the standard deviations of x and y respectively, and $\text{Cov}(x,y)$ denotes the covariance. Also, note that the variances of x and y are denoted by σ_x^2 and σ_y^2 . If the measurements are correlated, then the variance of their sum is equal to the sum of their variances plus two times the sum of all the covariances between distinct pairs of measurements. Again, the standard deviation is the square root of this quantity.

To get the geometric interpretation of covariance consider ϵ_i and δ_i of (B.1.1). The covariance between ϵ_i and δ_i is the cosine of the angle between ϵ_i and δ_i multiplied by their respective Euclidian lengths. Hence, the correlation coefficient is the cosine of the angle between two sets of measurements, when they are considered as vectors.

For estimating and constructing process control charts for multivariate data, the variances and covariances are arranged into a matrix with the variances down the main diagonal and covariances off the diagonal. This matrix is called a variance-covariance matrix or more simply a covariance

matrix. The precision of the composition estimates, and the sensitivity of the process control charts, will depend on both how well the variance-covariance matrices can be estimated and on the magnitude of the estimates. Accounting for the variance-covariance structure of the data will permit the effective use of the information in the data for controlling the LFCM and will minimize the number of control errors.

The data will be obtained from analyses of samples from the major tanks and from instrumentation within the LFCM process. Mathematically accounting for all the sources of data and determining the variance-covariance structure appears complicated, but the approach to constructing control schemes and estimating oxide concentrations is conceptually simple. The process is modeled and the model is used to determine the variance-covariance structure of the data. The covariance matrices of the concentration estimates from the various tanks are functions of the covariance matrices of the data. Once the estimates of the oxide concentrations and their covariance matrix are obtained, they are used to construct process control schemes.

B.2 FPT ESTIMATION AND CONTROL SCHEMES

B.2.1 Correlated Estimates of Elemental Concentration

In order to determine the variances of and covariance between the estimates of the oxide concentrations, it is necessary to model the process concentration data that will be gathered during LFCM runs so that all the variances and covariances expected to exist in the data are accounted for in the model. The variances and covariances of the final oxide concentration estimates will be functions of all the variances and covariances in the data.

The covariances expected in the data will arise from three sources: the chemistry of the process, the sampling and analyzing of the waste/frit and glass slurries, and the heels left after each batch is processed in a particular tank.

The chemistry of the process will cause correlations because some oxide concentrations will be used to determine the concentrations of other oxides.

Also, oxides which dissolve will have random fluctuations in their concentrations that will be more similar to each other than to random fluctuations of the oxides that will behave as suspended solids. How the various elements will chemically react with each other in the waste/frit and glass slurries will cause correlations.

The sampling and analyzing of the materials sampled from the process will cause correlations to exist. The samples from the same batch of slurry will tend to be more alike than samples taken from other batches. The batches will differ from each other in chemical makeup. Samples from a common batch will exhibit the chemical properties of that batch. Likewise, the aliquots from a common sample will be more alike than aliquots from other samples. The multivariate random nested model is designed to handle these kinds of the correlations in the data.

The heels from each batch will cause the different batches of waste/frit slurry to be correlated. Since each batch of waste/frit slurry is composed of some of the slurry from previous batches, each batch contains information on the oxide composition of the previous batches. Hence, no batch is independent of the previous batches as far as information on composition is concerned. A univariate form of the multivariate random nested model is used to account for these correlations.

The variances and covariances will be summarized in four matrices. The variances and covariances of the composition measurements will be contained in a batch covariance matrix, a covariance matrix due to sampling and a covariance matrix due to analyzing the aliquots. The covariances due to the tank heels will be summarized in a matrix that is a function of the transition matrix which describes the relationship between the compositions of the different batches. The covariance matrices due to batches, samples and analyses will be denoted by the capital Greek letter sigma subscripted by B, S, and A, respectively. The heel covariance matrix will be denoted by PP' where P is the transition matrix, and PP' is the regular matrix product of P with its transpose.

B.2.2 Matrix Model of the Batching Process

Each batch of frit/waste slurry made in the FPT is composed of slurry from the previous batch due to the heel left in the FPT and slurry from a new mixture of frit/waste slurry (see Figure B.2). Let μ_{Fi} denote the true oxide concentrations of the i^{th} batch and let μ_{Ni} denote the true oxide concentrations of the new mixture of frit/waste slurry which has been added to the heel in the FPT from the $i-1^{\text{st}}$ batch to make up the i^{th} batch. Both μ_{Fi} and μ_{Ni} are $1 \times k$ row vectors where k is the number of oxides analyzed. From Figure B.2, let p_i denote the fraction of the total volume of the i^{th} batch corresponding to the heel volume left over from the $i-1^{\text{st}}$ batch. Then

$$\mu_{F1} = \mu_{N1}$$

$$\mu_{F2} = p_2 \mu_{N1} + (1-p_2) \mu_{N2}$$

$$\mu_{F3} = p_3 \mu_{F2} + (1-p_3) \mu_{N3}$$

$$= p_3 p_2 \mu_{N1} + p_3 (1-p_2) \mu_{N2} + (1-p_3) \mu_{N3}$$

If the μ_{Fi} and μ_{Ni} are collected into $n \times k$ matrices, M_F and M_N , then

$$M_F = P M_N \quad (\text{B.2.1})$$

where

$$P = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ p_2 & 1-p_2 & 0 & 0 & \dots & 0 \\ p_2 p_3 & p_3 (1-p_2) & 1-p_3 & 0 & 0 & 0 \\ p_2 p_3 p_4 & p_3 p_4 (1-p_2) & p_4 (1-p_3) & 1-p_4 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \prod_{i=2}^n p_i & (1-p_2) \prod_{i=3}^n p_i & (1-p_3) \prod_{i=4}^n p_i & (1-p_4) \prod_{i=5}^n p_i & \dots (1-p_j) \prod_{i=j+1}^n p_i & 1-p_n \end{bmatrix} \quad (\text{B.2.2})$$

FIGURE B.2. Sources of Frit/Waste Slurry in the FPT

P is an $n \times n$ lower triangular matrix with a nonzero determinant. Therefore, P is nonsingular and has an inverse P^{-1} . Hence, (B.2.1) can be rewritten

$$M_N = P^{-1} M_F \quad (\text{B.2.3})$$

Equations (B.2.1) and (B.2.3) express the relationship between the true oxide concentrations of the new frit/waste slurry coming into the FPT and the frit/waste slurry remaining in the FPT. Subscripts are used to label the μ_F and μ_N and p of each batch because they will vary from batch to batch.

The μ_{Fi} and μ_{Ni} will differ from batch to batch for several reasons. The frit additions will be calculated, based on sample estimates of the composition of the mixture of the new batch of waste and the heel of waste/frit slurry remaining from the previous batch, and these sample estimates will be subject to uncertainty due to sampling and analyzing the sample. The heel volumes will be measured with some uncertainty. Homogeneity of the mixture sampled will vary. Hence, the calculations of the amount of frit to add will yield estimates of the true amount of frit to add and not the true amounts themselves. Additionally, inaccuracies in the actual amounts of frit added will cause the batch compositions to vary. It is assumed that the frit will be measured out in some gross amount and not to some fraction of a milligram. These sources of variation in the compositions the batches are considered to be the chance fluctuations that cannot be traced to any one source. If the LFCM is in statistical control, then μ_{Fi} and μ_{Ni} will randomly fluctuate about the target composition μ_T .

The p_i in (B.2.2) are assumed to be the true fractions. The volume determinations used to estimate the p_i will vary because of imprecision in measuring the volumes. In practice, the total batch volume and heel volume measurements are expected to have relative standard deviations of 5 to 10% of the total batch volume. The volume measurement will be used to estimate the true volumes and the ratio of the estimates will be used to estimate p_i . The random variations in volume measurements can greatly affect the estimated values of the p_i . If the estimates of the p_i vary greatly, then they cannot be used to estimate the relationship given in (B.2.1). Equation (B.2.1) is not used in this report for prediction. However, it is needed for determining the variance-covariance structure of the data.

If there is no bias in the volume measurements, one remedy to the problem of estimating the p_i is to repeatedly obtain volume measurements and use the average tank volumes. If the total batch volume is 23,000 L and the heel volume is 3220 L (i.e., $p = 0.14$) and the standard deviation associated with a single volume measurement is 1150 L (%RSD = 5%), then the average of 57 volume measurements would have a percent relative standard deviation of 0.67% and one would be 99.7% confident that the true value of p would fall inside the interval from 0.12 to 0.16. If the number of volume measurements were 918 then the percent relative standard deviation of each average volume would be 0.17% and one would be 99.7% confident that the true value of p would fall between 0.135 and 0.145.

How precisely the p_i must be estimated will depend upon how sensitive (B.2.1) is to deviations from the true values of the p_i and on how precisely the glass composition must be known. The latter of these will be set by design specifications. The former can and should be ascertained by simulations. The dependence of the variance-covariance structure of the estimates of the composition of the frit/waste slurry in the FPT on the volume measurements can be reduced by making the value of the true p_i as small as possible. Obviously, there are practical limitations to this. So, in

practice the accuracy and precision of the estimated composition of the frit/waste slurry in the FPT and (as shown below) the MFT will depend upon the accuracy and precision of the volume measurements in those two tanks.

B.2.3 Matrix Model Incorporating the Sampling Structure

In order to determine the oxide concentrations of each batch, 's' samples are drawn from each batch and 'a' analyses are performed on each sample. The model for this sampling scheme is

$$C_{Fijl} = \mu_{Fi} + S_{(i)j} + A_{(ij)l} \quad (B.2.4)$$

where C_{Fijl} , μ_{Fi} , $S_{(i)j}$, and $A_{(ij)l}$ are all $1 \times k$ row vectors. $S_{(i)j}$ denotes the effect due to taking the j^{th} sample from the i^{th} batch (sample-to-sample variation) and $A_{(ij)l}$ denotes the l^{th} analysis performed on the j^{th} sample of the i^{th} batch (analytical variation). If there are 'b' batches, 's' samples per batch and 'a' analyses per sample then (B.2.4) can be rewritten in matrix notation:

$$C_F = M_F + S + A \quad (B.2.5)$$

where C_F , M_F , S , and A are $bsa \times k$ matrices and C_F contains the actual measured values. More specifically, where C_F , M_F , S , and A are $bsa \times k$ matrices and C_F contains the actual measured values.

$$M_F = C_b (\mu_{fi} \otimes j_s \otimes j_a)$$

$$S = C_b [C_s (S_{(i)j} \otimes j_a)]$$

and

$$A = C_b \{C_s [C_a (A_{(ij)l})]\}$$

where the notation $C_r (Q_i)$ denotes a matrix formed by stacking the n Q_i matrices on top of each other:

$$C_n(Q_i) = \begin{bmatrix} Q_1 \\ Q_2 \\ \vdots \\ Q_n \end{bmatrix}$$

If the Q_i are $m_i \times k$ matrices then $C_n(Q_i)$ is a $\sum_{i=1}^n m_i \times k$ matrix. The vectors j_s and j_a denote $s \times 1$ and $a \times 1$ vectors of ones. The notation $A \otimes B$ denotes the Kronecker product of A and B (see Appendix D). Substituting (B.2.1) into (B.2.5) gives

$$C_F = PM_N + S + A \quad (B.2.6)$$

If the LFCM process is in statistical control the μ_{Nj} , and hence, the μ_{Fj} , vary randomly about μ_T the vector of target concentrations. It is then possible to separate M_N into $j_{bsa} \otimes \mu_T$, and B where j_{bsa} is a $bsa \times 1$ vector of 1's and B is the $bsa \times k$ matrix of batch to batch effects and (B.2.6) becomes

$$C_F = j_{bsa} \otimes \mu_T + (P \otimes I_s \otimes I_a) B + S + A \quad (B.2.7)$$

It is assumed that the rows of B are independently and identically distributed with a mean vector of zeros and covariance matrix B . Similarly the rows of S and A are distributed with zero mean vectors and covariance matrices Σ_S and Σ_A , respectively. The matrix P accounts for the batch to batch correlations due to the heels. Equation (B.2.5) is useful for estimating the μ_{Fj} for each batch. Equation (B.2.7) is useful for estimating μ_T .

The form of Equation (B.2.7) does not permit one to write the entire covariance structure of C_F without doing it piecewise. Equation (B.2.7) can be rewritten in the form of a general linear regression model (see Appendix C). This is accomplished by reorganizing the 'k' columns of C_F ,

$j_{bsa} \otimes \mu_T$, B, S, and A on top of one another. Letting the subscript 'c' denote these new column vectors, (B.2.7) becomes

$$C_{Fc} = C_k(\mu_m j_{bsa}) + (I_k \otimes P \otimes I_s \otimes I_a) B_c + S_c + A_c \quad (B.2.8)$$

where $C_k(\mu_m j_{bsa})$ denotes each of the k elements of μ_T (subscripted by the letter m, multiplied by j_{bsa} and stacked on top of each other). If the matrix P in (B.2.8) were replaced with I_b , then (B.2.8) would be a multivariate random two-fold nested model; the variance-covariance structure of this model forms the basis of the variance-covariance matrices for the FPT and MFT data and is developed in greater detail in Appendix C.

The variance-covariance matrix of C_{Fc} is

$$\Sigma_{C_{Fc}} = \Sigma_B \otimes PP' \otimes J_s \otimes J_a + \Sigma_s \otimes I_b \otimes I_s \otimes J_a + \Sigma_A \otimes I_b \otimes I_s \otimes I_a \quad (B.2.9)$$

where J_s is a $s \times s$ matrix of ones, J_a is an $a \times a$ matrix of ones, and I_b , I_s and I_a are identity matrices of dimension $b \times b$, $s \times s$ and $a \times a$, respectively. Equation (B.2.9) is the multivariate extension of the univariate model (see Hocking 1985, for a discussion of the univariate model).

The batch means for each of the k constituents are estimated by

$$\hat{M}_{Fc} = \frac{1}{sa} (I_k \otimes I_b \otimes j_s \otimes j_a)' C_{Fc} \quad (B.2.10)$$

where j_s and j_a are $s \times 1$ and $a \times 1$ vectors of ones respectively.

The variance-covariance matrix of M_{Fc} is

$$\begin{aligned} \Sigma_{\hat{M}_{Fc}} &= \frac{1}{sa} (I_k \otimes I_b \otimes j_s \otimes j_a)' \Sigma_{C_{Fc}} (I_k \otimes I_b \otimes j_s \otimes j_a) \\ &= \Sigma_B \otimes PP' + \frac{1}{s} \Sigma_s \otimes I_b + \frac{1}{sa} \Sigma_A \otimes I_b \end{aligned}$$

$$= \Sigma_B \otimes PP' + \left(\frac{1}{s} \Sigma_S + \frac{1}{s_a} \Sigma_A \right) \otimes I_b \quad (\text{B.2.11})$$

The covariance matrices Σ_B , Σ_S and Σ_A can be estimated using (B.2.6) or (B.2.7) and standard multivariate analysis of variance methods. However, the estimate of Σ_B will need to be multiplied by $b/\text{trace}(PP')$ to correct for the bias induced by the presence of PP' in the covariance structure.

One last point to be made about the estimation of Σ_B , Σ_S , and Σ_A regards the required number of batches, samples per batch and analyses per sample as on the FPT to estimate these matrices. Having broken down the actual measured elemental concentrations (C_{FC}) into the individual explainable effects plus a random unknown effect, and having derived an expression for the variance of C_{FC} , we can move onto estimating parameters of interest and estimating the variances associated with each of those parameters.

B.2.4 Estimating the FPT Batch Averages and Uncertainties

During waste glass production, it is important that the average elemental concentrations for each batch vary within an allowable range around the target feed composition. To statistically monitor the fluctuations around the target feed composition for each batch, one must estimate the average batch composition and the variance-covariance matrix of the estimated average. In order to estimate the variance-covariance matrix of the estimated batch averages, Σ_B , Σ_S and Σ_A need to be estimated. But Σ_B , Σ_S , and Σ_A are $k \times k$ covariance matrices and cannot be estimated unless b , s , and a are greater than or equal to certain values which are functions of k , b and s . These values are summarized in Table B.1. Numerical examples of the sizes of ' b ', ' s ', and ' a ' needed to estimate Σ_B , Σ_S , and Σ_A as data is accumulated during LFCM runs are given in Table B.2. Note that in Table B.2, Σ_B is not estimable until $b > k$.

B.2.5 Statistical Process Control for the FPT

Although process control schemes may be more useful when applied to the MFT, it is possible to construct control schemes for the FPT which may prove valuable. These schemes are based on a statistic called Hotelling's

TABLE B.1. Sample Sizes and Estimability of Σ_B , Σ_S , and Σ_A Where 'ne' Signifies Not Estimable and 'e' Signifies Estimable

<u>b</u>	<u>s</u>	<u>a</u>	<u>Σ_B</u>	<u>Σ_S</u>	<u>Σ_A</u>
$< k+1$	$< \frac{k+1}{b}$	$< \frac{k+1}{bs}$	ne	ne	ne
$< k+1$	$< \frac{k+1}{b}$	$> \frac{k+1}{bs}$	ne	ne	e
$< k+1$	$\geq \frac{k+1}{b}$	≥ 2	ne	e	e
$\geq k+1$	≥ 2	≥ 2	e	e	e

TABLE B.2. Required Number of Batches (b), Samples per Batch (s), and Analysis Per Sample (a) to Estimate Σ_S and Σ_A When the Number of Elemental Constituents (k) is 16 and 32

<u>K=16</u>			<u>K=32</u>		
<u>b</u>	<u>s</u>	<u>a</u>	<u>b</u>	<u>s</u>	<u>a</u>
1	≥ 17	≥ 2	1	≥ 33	≥ 2
2	≥ 9	≥ 2	2	≥ 17	≥ 2
4	≥ 5	≥ 2	4	≥ 9	≥ 2
8	≥ 3	≥ 2	12	≥ 5	≥ 2
12	≥ 2	≥ 2	16	≥ 4	≥ 2
16	≥ 2	≥ 2	20	≥ 3	≥ 2
> 16	≥ 2	≥ 2	24	≥ 3	≥ 2
			28	≥ 2	≥ 2
			32	≥ 2	≥ 2
			> 32	≥ 2	≥ 2

T^2 -statistic which will be presented below. Two possible control schemes are presented along with their advantages and disadvantages.

B.2.5.1 Controlling the Process to Have an Acceptable Variation Between Batches

The frit/waste slurry composition can be monitored by constructing a control chart for the estimated batch composition. $\hat{\mu}_{Fi}$ represents the $k \times 1$ vector of oxide concentration estimates for the i^{th} batch of the FPT.

$$T_i^2 = (\hat{\mu}_{Fi} - \mu_T)' \hat{\Sigma}_F^{-1} (\hat{\mu}_{Fi} - \mu_T) \quad (\text{B.2.12})$$

$$\hat{\Sigma}_F = p_{ij} \hat{\Sigma}_B + \frac{1}{s} \hat{\Sigma}_S + \frac{1}{sa} \hat{\Sigma}_A$$

where the '^' indicate the estimate of the corresponding covariance matrix and p_{ij} is the i^{th} diagonal element of PP' . T_i^2 will be approximately distributed as a Hotelling's T^2 distribution of dimension k and degrees of freedom ν . Currently methods for calculating parameter ν for (B.2.12) do not exist although approximations based on univariate methods are being considered. Obviously, ν ranges between 0 and b_{sa} . It is assumed that ν is approximately equal to $b-1$ and that a control chart based on this number of degrees of freedom will be approximately correct.

The process control chart would consist of plotting T^2 with limits set using the Hotelling T^2 distribution. It will detect individual batches that are too far from the target composition to be acceptable. If an out of control batch is detected then various univariate tests and discriminate functions can be used to find which constituent concentrations are out of control and corrective action can be taken. It should be noted that the T_i^2 will not be statistically independent. Therefore, rules about the number of runs above or below the expected value of T^2 would not be valid. Each batch composition would be tested without reference to other batches.

If the FPT is in statistical control, i.e., the oxide concentrations are acceptable, and the number of batches of slurry which have been processed is

greater than the number of oxides being monitored, then the batch-to-batch covariance matrix can be estimated and (B.2.12) can be used to monitor the slurry composition in the FPT. If the initial FPT batches are not acceptable, the estimated batch-to-batch variances and covariances will be unacceptably large. This unacceptable estimate of the batch-to-batch covariance matrix should not be used in (B.2.12) to determine whether the process is in statistical control. Only when the covariance matrix is estimated from data obtained when the process is in statistical control can (B.2.12) be implemented. This problem can be remedied in part, if acceptable upper bounds for the variances can be determined. These acceptable variances could then be used to construct the covariance matrix for the batch-to-batch variability. This would also be a solution for the case when not enough batches of slurry have been processed to estimate the batch-to-batch covariance matrix.

A statistical control chart of the calculated T_i^2 values will detect unacceptable shifts from the target composition. It is also possible that the batch, sampling, or analytical uncertainties could increase without a shift from the target composition. Changes in process variations would signal an out-of-control or unstable process. Control schemes for detecting process variation changes are available but are not addressed herein.

B.2.5.2 Controlling Batch Variation to Zero

The process control scheme outlined above allowed for an acceptable batch-to-batch variation in composition. A second control scheme is to control the process such that the batch-to-batch variability is zero. To construct this chart calculate

$$T_i^2 = (\hat{\mu}_{Fi}' - \mu_T') \hat{\Sigma}^{-1} (\hat{\mu}_{Fi}' - \mu_T') \quad (\text{B.2.13})$$

where

$$\hat{\Sigma} = \frac{1}{s} \hat{\Sigma}_s + \frac{1}{sa} \hat{\Sigma}_A$$

If the batch-to-batch differences are zero, then the T_j^2 are independent and distributed as a Hotelling T^2 -distribution with dimension k and $\nu = s-1$, where it is assumed that $s-1 > k$. If $s-1$ is not greater than k , then the data can be pooled across batches and ν will be $b(s-1)$. If the data are pooled across batches, then T will no longer be statistically independent, but they may still be used in a control chart if they are compared against their respective critical value and no rules about runs above a certain value are used. When a T_j^2 exceeds its critical value, then the process is considered out of statistical control and it is stopped. The confidence intervals and the discriminant function can be examined for that batch to determine if one of the constituents has an anomalous concentration. Past process data and composition data can be analyzed using principal component analysis, canonical correlation analysis, discriminant analysis, etc. to examine the relationships between the process parameters and the batch compositions in order to find out why the process went out of control.

As depicted in Equation (B.2.13), to set up a control scheme which does not allow for any batch-to-batch variations, it is not necessary to estimate Σ_B . This eliminates problems due to the batch-to-batch correlations encountered when using (B.2.12) to control the process. Although the statistical problem becomes much simpler, control charts based on (B.2.13) result in a very stringent control scheme.

If the batch-to-batch variations are much larger than the sample-to-sample variations, (B.2.13) will declare most batches unacceptable until operators actually control the system so that there are no batch-to-batch variations. This may not be a realistic option.

Statistical process control schemes can be used in two ways. One use of control schemes is to maintain the current level of performance of a process. A second use of control schemes is to improve process performance. Equation (B.2.12) fits the first of these, while (B.2.13) fits the second. If the characteristics of the waste entering the LFCM system are such that it is practical to try to reduce the batch-to-batch variability to zero then (B.2.13) will be a useful tool.

As a passing note, two things that would help reduce batch-to-batch variability are mentioned. First, the number of waste samples must be sufficiently large so that the waste composition is well defined in order to know precisely the proper frit addition recipe. Second, precise determination of the actual amounts of the frit constituents added to the waste are needed. The first of these will reduce errors in prescribing the "right" frit recipe. The larger the number of waste samples, the more precisely the true waste composition will be known and the more closely the prescribed frit will match the waste. The second suggestion will help insure that the "right" frit is actually made instead of "something close." Obviously, there are practical limitations to these suggestions, but to the extent they are implemented the batch-to-batch variability will be smaller. Simulations could be done to determine the point of diminishing returns.

The control schemes given by (B.2.12) and (B.2.13) both are based on the assumption that the data follow a multivariate normal distribution. It turns out, however, that like the student's t-test of a single mean, T^2 is robust to departures from this assumption.

B.3 MFT ESTIMATION AND CONTROL SCHEMES

Process control at the MFT is similar to that at the FPT except that some additional control charts can be constructed. Like the FPT the MFT is a batch fed tank and the relationship between batches is the same as that illustrated for the FPT in Figure B.1. Equation (B.2.1) can be used to estimate the MFT batch averages:

$$\begin{aligned} M_M &= P_M M_F \\ &= P_M P_F M_N \end{aligned} \tag{B.3.1}$$

where the subscripts M and F have been used to identify the MFT and FPT, respectively. P_M is similar to P_F and its elements are described by (B.2.2).

The MFT is batch fed from the FPT and each MFT batch is sampled with each sample analyzed several times just as in the case of the FPT.

Therefore, Equations (B.2.1 to B.2.13) can be used to model, estimate concentrations and construct control charts based only on the data from the MFT by replacing P with $P_M P_F$, P^{-1} with $P_F^{-1} P_M^{-1}$, PP' with $P_M P_F P_F' P_M'$, $P^{-1} P^{-1'}$ with $P_F^{-1} P_M^{-1} P_M^{-1} P_F^{-1'}$ and C_{FC} with C_{MC} where they occur in those equations. Also, the estimate of Σ_B based on the MFT data must be multiplied by $b/\text{tr}(P_M P_F P_F' P_M')$ instead of $b/\text{tr}(P_F P_F')$.

Two additional control schemes are presented below. Both of these schemes involve the prediction of the MFT concentrations based on FPT data. The first scheme involves monitoring the MFT by watching the differences between estimates of MFT concentrations based on FPT data and estimates of MFT concentrations based on averages of MFT samples. In the second scheme, data from the FPT and data from the MFT are combined to get a single estimate of the MFT concentrations, and then control charts are constructed.

B.3.1 Estimation of the MFT Average Concentrations (M_{FC})

From (B.3.1) one has

$$\begin{aligned} M_{MC} &= (I_k \otimes P_M) M_{FC} \\ &= (I_k \otimes P_M P_F) M_{NC} \end{aligned} \quad (B.3.2)$$

The best estimate of M_{MC} based on the FPT data is to substitute the estimate of the average concentrations in the FPT from Equation (B.2.10) into (B.3.2):

$$\hat{M}_{MC} = (I_k \otimes P_M) \hat{M}_{FC} \quad (B.3.3)$$

The variance-covariance matrix of $\hat{M}_{MC}$ can be estimated as

$$\begin{aligned} \hat{\Sigma}_{M_{FC}} &= (I_k \otimes P_M) \hat{\Sigma}_{M_{FC}} (I \otimes P_M') \\ &= \Sigma_B \otimes P_M P_F P_F' P_M' + \frac{1}{s} \Sigma_S \otimes P_M P_M' + \frac{1}{sa} \Sigma_A \otimes P_M P_M' \\ &= \Sigma_B \otimes P_M P_F P_F' P_M' + \left(\frac{1}{s} \Sigma_S + \frac{1}{sa} \Sigma_A \right) \otimes P_M P_M' \end{aligned} \quad (B.3.3)$$

The estimates of Σ_B , Σ_S , and Σ_A are obtained by combining the corresponding estimates from the analysis of the FPT data and MFT data.

The estimate of M_{MC} based on MFT data and its covariance matrix are

$$\hat{M}_{MC} = \frac{1}{sa} (I_k \otimes I_b \otimes j'_s \otimes j'_a) C_{MC} \quad (B.3.5)$$

and

$$\begin{aligned} \Sigma_{\hat{M}_{MC}} &= \Sigma_B \otimes P_M P_F P'_F P'_M + \frac{1}{s} \Sigma_S \otimes I_b + \frac{1}{sa} \Sigma_A \otimes I_b \\ &= \Sigma_B \otimes P_M P_F P'_F P'_M + \left(\frac{1}{s} \Sigma_S + \frac{1}{sa} \Sigma_A \right) \otimes I_b \end{aligned} \quad (B.3.6)$$

where it is assumed that the number of samples and analyses per sample are the same for both the FPT and the MFT. Also, it is assumed that Σ_B , Σ_S , and Σ_A remain constant from tank to tank. P_F appears in (B.3.6) because M_{MC} is a function of M_{NC} and it is the covariance structure of the new batches being added to the heels in the FPT that is used as the basis for the covariance matrices.

B.3.2 Process Control on Differences Between Two Estimates of MFT Composition

In Section B.3.1 two possible estimates of the MFT average concentrations for each batch, $\hat{M}_{MC}$ and $\bar{M}_{MC}$ were derived. Control schemes based on the difference between the predicted MFT concentrations using FPT data and the predicted MFT concentrations using the MFT data can be useful for detecting problems between the time the FPT measurements were obtained and the time the MFT measurements were obtained.

Let D denote the difference between (B.3.3) and (B.3.5):

$$D = \hat{M}_{MC} - \bar{M}_{MC} \quad (B.3.7)$$

The covariance matrix for D is

$$\begin{aligned}
 \Sigma_D &= \Sigma_{\hat{M}_{MC}} + \Sigma_{\hat{M}_{MC}} - 2 \text{Cov}(\hat{M}_{MC}, \hat{M}_{MC}) \\
 &= \Sigma_B \otimes P_M P_F P_F' P_M' + \left(\frac{1}{s} \Sigma_S + \frac{1}{sa} \Sigma_A \right) \otimes I_b \\
 &\quad + \Sigma_B \otimes P_M P_F P_F' P_M' + \left(\frac{1}{s} \Sigma_S + \frac{1}{sa} \Sigma_A \right) \otimes P_M P_M' \\
 &\quad - 2 \Sigma_B \otimes P_M P_F P_F' P_M' \\
 &= \frac{1}{s} \Sigma_S + \frac{1}{sa} \Sigma_A \otimes (I_b + P_M P_M') \tag{B.3.8}
 \end{aligned}$$

Let $1 + p_{ii}$ denote the i^{th} diagonal element of $I_b + P_M P_M'$. Then

$$T_i^2 = D_i' \Sigma_{Di} D_i \tag{B.3.9}$$

where

$$\Sigma_{Di} = (p_{ii} + 1) \left(\frac{1}{s} \Sigma_S + \frac{1}{sa} \Sigma_A \right)$$

and D_i is the $k \times 1$ vector of differences for the i^{th} batch. T_i^2 will have a Hotelling T^2 -distribution with dimension k and $\nu = b(s-1)$. The T_i^2 of (B.3.9) are correlated as indicated by (B.3.8). Thus, out of control rules such as seven T_i^2 values in a row above a certain value could not be used. However, the general rule of detecting out of control processes by charting each T_i^2 could be used to judge each batch separately. Again, if the multivariate T^2 control chart detects an out of control batch, univariate tests and discriminant functions could be examined to determine which constituents are out of control.

B.3.3 Process Control on Combined FPT and MFT Estimate of MFT Composition

If the two predicted MFT concentration vectors, $\hat{M}_{MC}$ and $\hat{M}_{MC}$, are not significantly different, then a more precise estimate of M_{MC} can be obtained

by combining the information in the two estimates into a single estimate. To do this consider the following regression model

$$\begin{bmatrix} \bar{M}_{MC} \\ \hat{M}_{MC} \end{bmatrix} = \begin{bmatrix} I_k \otimes I_b \\ I_k \otimes I_b \end{bmatrix} M_{MC} + \begin{bmatrix} E_{\bar{M}_{MC}} \\ E_{\hat{M}_{MC}} \end{bmatrix} \quad (\text{B.3.10})$$

where the two column estimates of M_{MC} are stacked on top of each other and for simplicity the random errors due to batches, sampling, and analysis are denoted by $E_{\bar{M}_{MC}}$ and $E_{\hat{M}_{MC}}$. Note that (B.3.10) has the usual regression form of

$$y = X\beta + E \quad (\text{B.3.11})$$

If the covariance matrix of E in (B.3.11) is $\sigma^2 I$ then the best estimate of β is

$$\hat{\beta} = (X'X)^{-1} X' y \quad (\text{B.3.12})$$

where best refers to minimum variance among all possible linear unbiased estimators of β . If however, the covariance matrix of E in (B.3.11) is Σ instead of $\sigma^2 I$ then (B.3.12) is no longer the minimum variance estimator, but

$$\hat{\beta} = (X' \Sigma^{-1} X)^{-1} X' \Sigma^{-1} y \quad (\text{B.3.13})$$

is the best estimator (Judge et al. 1982). Equation (B.3.13) will reduce to the form of (B.3.12) if $X = I \otimes Z$ and $\Sigma = \Omega \otimes I$ (see Appendix C). However, in the present case the combined estimator of M_{MC} will have the form of (B.3.13).

The covariance matrix of (B.3.10) is

$$\Sigma_E = \begin{bmatrix} \Sigma_B \otimes P_M P_F P_F' P_M' + \frac{1}{s} \Sigma_S + \frac{1}{sa} \Sigma_A \otimes I_b & \Sigma_B \otimes P_M P_F P_F' P_M' \\ \Sigma_B \otimes P_M P_F P_F' P_M' & \Sigma_B \otimes P_M P_F P_F' P_M' + \frac{1}{s} \Sigma_S + \frac{1}{sa} \Sigma_A \otimes P_M P_M' \end{bmatrix} \quad (B.3.14)$$

Σ_E is a $2kb \times 2kb$ matrix. The matrix in (B.3.10) corresponding to X in (B.3.11) is

$$\begin{bmatrix} I_k \otimes I_b \\ I_k \otimes I_b \end{bmatrix} = \begin{bmatrix} I_{kb} \\ I_{kb} \end{bmatrix} \quad (B.3.15)$$

and M_{Mc} corresponds to β . Therefore, the best estimate of M_{Mc} is

$$M_{Mc}^* = \left(\begin{bmatrix} I_{kb} \\ [I_{kb}, I_{kb}] \Sigma_E^{-1} \end{bmatrix} \begin{bmatrix} I_{kb} \\ I_{kb} \end{bmatrix} \right)^{-1} \begin{bmatrix} I_{kb}, I_{kb} \end{bmatrix} \Sigma_E^{-1} \begin{bmatrix} M_{Mc} \\ \hat{M}_{Mc} \end{bmatrix} \quad (B.3.16)$$

The covariance matrix of $\hat{M}_{Mc}$ is

$$\Sigma_{M_{Mc}^*} = \left(\begin{bmatrix} I_{kb} \\ [I_{kb}, I_{kb}] \Sigma_E^{-1} \end{bmatrix} \begin{bmatrix} I_{kb} \\ I_{kb} \end{bmatrix} \right)^{-1} \quad (B.3.17)$$

Equations (B.3.16) and (B.3.17) can be expanded as follows: Let

$$\Sigma_{11} = \Sigma_B \otimes P_M P_F P_F' P_M' + \left(\frac{1}{s} \Sigma_S + \frac{1}{sa} \Sigma_A \right) \otimes I_b$$

$$\Sigma_{12} = \Sigma_B \otimes P_M P_F P'_F P'_M$$

$$\Sigma_{21} = \Sigma_{12}$$

$$\Sigma_{22} = \Sigma_B \otimes P_M P_F P'_F P'_M + \left(\frac{1}{s} \Sigma_s + \frac{1}{sa} \Sigma_A\right) \otimes P_M P'_M$$

Then

$$\Sigma_E = \begin{bmatrix} \Sigma_{11} & \Sigma_{12} \\ \Sigma_{21} & \Sigma_{22} \end{bmatrix}$$

and

$$\Sigma_E^{-1} = \begin{bmatrix} (\Sigma_{11} - \Sigma_{12} \Sigma_{22}^{-1} \Sigma_{21})^{-1} & -\Sigma_{11}^{-1} \Sigma_{12} (\Sigma_{22} - \Sigma_{21} \Sigma_{11}^{-1} \Sigma_{12})^{-1} \\ -\Sigma_{22}^{-1} \Sigma_{21} (\Sigma_{11} - \Sigma_{12} \Sigma_{22}^{-1} \Sigma_{21})^{-1} & (\Sigma_{22} - \Sigma_{21} \Sigma_{11}^{-1} \Sigma_{12})^{-1} \end{bmatrix}$$

(Graybill 1976).

$$\Sigma_{Mc}^* = [(I - \Sigma_{22}^{-1} \Sigma_{21})(\Sigma_{11} - \Sigma_{12} \Sigma_{22}^{-1} \Sigma_{21})^{-1} + (I - \Sigma_{11}^{-1} \Sigma_{12})(\Sigma_{22} - \Sigma_{21} \Sigma_{11}^{-1} \Sigma_{12})]^{-1}$$

$$\begin{aligned} \hat{M}_{Mc}^* &= \Sigma_{Mc}^* [(I - \Sigma_{22}^{-1} \Sigma_{21})(\Sigma_{11} - \Sigma_{12} \Sigma_{22}^{-1} \Sigma_{21})^{-1} \hat{M}_{Mc} \\ &+ (I - \Sigma_{11}^{-1} \Sigma_{12})(\Sigma_{22} - \Sigma_{21} \Sigma_{11}^{-1} \Sigma_{12})^{-1} \hat{M}_{Mc}] \end{aligned}$$

$\hat{M}_{Mc}$ is a $kb \times i$ vector of all the batch means of all the constituents.

Let

$$\hat{M}_M^* = (j'_k \otimes I_b) [(\hat{M}_{Mc}^* j'_k) \cdot (I_k \otimes j_b)]$$

$\hat{M}_M$ is a $b \times k$ matrix of the 'b' batch mean vectors: the i^{th} row of $\hat{M}_M$ contains the 'k' constituent means for the i^{th} batch.

The covariance matrix of the i^{th} batch mean vector is pulled out of Σ_{MM}^* as follows. Let j_z be a $b \times 1$ vector whose elements are all zero except the i^{th} element which is equal to one. Let Σ_{Mi}^* denote the covariance matrix of the vector of means of i^{th} batch. Then

$$\Sigma_{Mi}^* = (I_k \otimes j_z') \Sigma_{MM}^* (I_k \otimes j_z)$$

Letting $i = 6$, Σ_{Mb}^* and the 6th row of $\hat{M}_M$ can be used for control charts or confidence intervals. Σ_{Mi}^* is estimated by estimating Σ_{11} , Σ_{12} , Σ_{21} and Σ_{22} of Σ_e and carrying through with the above calculations.

The exact degrees of freedom of $\hat{\Sigma}_E$ and Σ_{Mi}^* are unknown, but it is assumed that the degrees of freedom are close to $b-1$.

If no batch-to-batch variation is permitted then Equation (B.3.14) reduces to

$$\Sigma_e = \begin{bmatrix} \left(\frac{1}{s} \Sigma_s + \frac{1}{sa} \Sigma_a \right) \otimes I_b & Z \\ Z & \left(\frac{1}{s} \Sigma_s + \frac{1}{sa} \Sigma_a \right) \otimes P_M P_M' \end{bmatrix}$$

where Z is a $kb \times kb$ matrix of zeros. If no batch-to-batch variation is permitted, then the sensitivity of the control scheme is increased by increasing s , the number of samples.

The elements of (B.3.16) and (B.3.17) could be used to construct T^2 statistics and hence control schemes. At this time there is no method for determining the degrees of freedom, ν . However, the lower bound on ν is $b-1$ which can be used as a conservative estimate.

The minimum variance property of (B.3.16) holds as long as Σ_{ϵ} is known and not estimated. When Σ_{ϵ} is estimated (B.3.16) will have variance less than or equal to the estimator with the form of (B.3.12).

In summary, statistical process control methods have been demonstrated for the MFT. Four control schemes are possible: 1) monitor the measured MFT composition allowing for batch-to-batch variation 2) monitor the MFT composition not allowing for batch-to-batch variation, 3) monitor the combined MFT and FPT estimate of the MFT composition, and 4) monitor the difference between the measured MFT composition and the predicted MFT composition from FPT measurements. Each of the four control schemes is tailored to meet different controlling objectives and is more sensitive to different types of process shifts. Next, we turn our attention to process control on the melter.

B.4 MELTER

The melter is continuously fed a frit/waste slurry from the MFT. As a result a differential equation is used to model the concentrations of the glass slurry in the melter. This model will be explained for a single constituent and then the matrix form of the model which includes all of the constituents will be given.

B.4.1 Single Constituent Model

The melter is continuously fed by a stream of frit/waste slurry from the MFT. When the volume of slurry in the MFT drops to a certain level, the tank is refilled with a new batch of slurry from the FPT. The elemental concentrations in the new batch will not be the same as the concentrations in the previous batch. Thus, the elemental concentrations in the MFT undergo a step change as the new batch is mixed with the remainder of the previous batch.

Since the melter is being fed continuously, after the MFT has received a new batch of slurry, the concentrations of the glass components in the melter gradually change toward the concentrations in the new MFT batch (see Figure B.3). If the melter could be fed by a single MFT batch for a

FIGURE B.3. Elemental Concentration in the MFT and Melter

sufficiently long period, the elemental concentrations in the melter would eventually be equal to the concentrations in the MFT.

If it is assumed that the slurry in the MFT is perfectly mixed and that the melter functions as a single well-mixed tank, then the concentration of a single elemental component in the glass leaving the melter can be represented as a function of time with the following differential equation:

$$FC_0 = FC + V \frac{dC}{dt} \quad (B.4.1)$$

$$\text{where } C_0 = C_f - C_i \quad (B.4.2)$$

$$C = C_t - C_i \quad (B.4.3)$$

C_t = elemental composition of the glass leaving the melter at any time t after the new batch is started

C_i = initial glass composition in the melter

C_f = final glass composition that would leave the melter at infinite time. This is also the composition of the feed batch.

V = volume of glass in the melter (liters)

F = volumetric flow rate of the feed (as a glass)

t = time since the new feed batch was started (in hours).

These concentrations are in the units of grams of element per unit volume of glass in liters. Similarly, the volumetric flow rate of the feed is in liters of glass per hour. The above concentrations can be given in units of mass per volume of feed instead of volume of glass. In this case, the concentrations must be multiplied by the ratio of the glass density to the feed density and the covariance matrix of the estimates of the batch concentrations must be multiplied by the square of this ratio.

The solution to (B.4.1) for a step change in C_0 is:

$$C = C_0 \left[1 - e^{-\frac{t F}{V}} \right] \quad (\text{B.4.4})$$

Substituting (B.4.2) and (B.4.3) into (B.4.4), rearranging and simplifying one can represent the melter content for the n^{th} batch as

$$C_{t,n} = C_{f,n} \left[1 - e^{-\frac{t F_n}{V_n}} \right] + C_{i,n} e^{-\frac{t F_n}{V_n}} \quad (\text{B.4.5})$$

Equation (B.4.5) gives the concentration of a single constituent in the melter at some time t after the MFT received a new batch of slurry from the FPT. $\hat{C}_{t,n}$ provides an estimate of the glass composition being poured into a canister at a specific time as the n^{th} MFT batch is being fed into the melter.

An estimate of $C_{f,n}$ in Equation (B.4.5) will be available from analyses of the MFT samples. However, the melter concentration at the beginning of a new MFT batch ($C_{i,n}$) cannot be directly obtained. If T_n denotes the time (hours) between the transfers to the MFT of the n^{th} and the $(n+1)^{\text{th}}$ batch, then $C_{i,n} = C_{T,n-1} = C_{t,n-1}$. Using the mass balance model of Equation (B.4.5) one can express $C_{i,n}$ as

$$C_{i,n} = C_{f,n-1} \left[1 - e^{-\frac{T_{n-1} F_{n-1}}{V_{n-1}}} \right] + C_{i,n-1} e^{-\frac{T_{n-1} F_{n-1}}{V_{n-1}}} \quad (\text{B.4.6})$$

Again, $C_{i,n-1}$ will not be directly measured but can be estimated from

$$C_{i,n-1} = C_{f,n-2} \left[1 - e^{-\frac{T_{n-2} F_{n-2}}{V_{n-2}}} \right] + C_{i,n-2} e^{-\frac{T_{n-2} F_{n-2}}{V_{n-2}}} \quad (\text{B.4.7})$$

Substituting (B.4.6) and (B.4.7) into (B.4.5) gives:

$$\begin{aligned} \hat{C}_{t,n} = & C_{f,n} \left[1 - e^{-\frac{tF_n}{V_n}} \right] + C_{f,n-1} \left[1 - e^{-\frac{T_{n-1} F_{n-1}}{V_{n-1}}} \right] e^{-\frac{tF_n}{V_n}} \\ & + C_{f,n-2} \left[1 - e^{-\frac{T_{n-2} F_{n-2}}{V_{n-2}}} \right] e^{-\frac{T_{n-1} F_{n-1}}{V_{n-1}}} e^{-\frac{tF_n}{V_n}} \end{aligned}$$

$$+ C_{i,n-2} \left[1 - e^{-\frac{T_{n-2} F_{n-2}}{V_{n-2}}} \right] e^{-\frac{T_{n-1} F_{n-1}}{V_{n-1}}} e^{-\frac{t F_n}{V_n}} \quad (B.4.8)$$

Recursively substituting for the remaining $C_{i,n-k}$ in Equation (B.4.8) yields

$$\begin{aligned} \hat{C}_{t,n} = & C_{f,n} \left[1 - e^{-\frac{t F_n}{V_n}} \right] + C_{f,n-1} \left[1 - e^{-\frac{T_{n-1} F_{n-1}}{V_{n-1}}} \right] e^{-\frac{t F_n}{V_n}} \\ & + \sum_{i=2}^{n-1} C_{f,n-i} \left[1 - e^{-\frac{T_{n-i} F_{n-i}}{V_{n-i}}} \right] e^{-\sum_{j=1}^{i-1} \frac{T_{n-j} F_{n-j}}{V_{n-j}}} e^{-\frac{t F_n}{V_n}} \end{aligned} \quad (B.4.9)$$

To derive the covariance matrix of the predicted glass composition, the model must be defined in terms of the variables which will actually be measured. Concentrations of the feed batch will be expressed in grams of element per liter of feed. The feed flow rate will be reported in liters of feed per hour. Conversion of these measured values to units appropriate for the model requires knowing the oxide loading in the feed and the density of the glass. To determine the oxide loading, an aliquot of the feed is dried, melted, and weighed. The oxide loading can vary from batch-to-batch and must therefore be accounted for in the model. The glass density is assumed to be constant and independent of the glass composition. Time measurements are assumed to have been known precisely.

The model for predicting the concentration of a given element in the melter after t hours of feeding the melter with the n^{th} MFT batch is shown below.

$$\begin{aligned}
\hat{C}_{t,n} = & C_{f,n} \left[1 - e^{-\frac{tM_n V_{f,n}}{\rho V_{s,n} V_n}} \right] + \\
& C_{f,n-1} \left[1 - e^{-\frac{T_{n-1} M_{n-1} V_{f,n-1}}{\rho V_{s,n-1} V_{n-1}}} \right] e^{-\frac{tM_n V_{f,n}}{\rho V_{s,n} V_n}} + \\
& \sum_{i=2}^{n-1} C_{f,n-i} \left[1 - e^{-\frac{T_{n-i} M_{n-i} V_{f,n-i}}{\rho V_{s,n-i} V_{n-i}}} \right] e^{-\frac{tM_n V_{f,n}}{\rho V_{s,n} V_n}} e^{-\sum_{j=1}^{i-1} \frac{T_{n-j} M_{n-j} V_{f,n-j}}{\rho V_{s,n-j} V_{n-j}}}
\end{aligned} \tag{B.4.10}$$

where $C_{f,i}$ = the elemental concentration in the i^{th} MFT batch (g/L)

M_i = the weight of the melted feed sample (g)

$V_{f,i}$ = the volumetric flow rate of the feed into melter (L/h)

$V_{s,i}$ = the volume of the feed sample before meltdown (mL)

T = time between batching into the MFT (h)

ρ = the density of the glass (g/mL)

V_i = the volume of material in the melter (L).

B.4.2 Multiple Constituent Model

The single constituent model of (B.4.10) is easily changed into a multiple constituent model using matrices, the Hadamard product of matrices (element wise multiplication of matrices: see Appendix D), and the Kronecker and regular products of matrices. First, Equation (B.4.10) will be represented with matrices for a single constituent then extended for multiple constituents.

Let C_{M_i} be the $b \times 1$ vector of MFT batch means for the i^{th} constituent (C_{M_i} was referred to as M_{M_i} in Section B.3).

Also, define the following vectors.

$$T = \begin{bmatrix} T_1 \\ \vdots \\ T_{b-1} \\ t \end{bmatrix} \quad M = \begin{bmatrix} M_1 \\ \vdots \\ M_b \end{bmatrix} \quad V_f = \begin{bmatrix} V_{f1} \\ \vdots \\ V_{fb} \end{bmatrix} \quad V_s = \begin{bmatrix} V_{s1} \\ \vdots \\ V_{sb} \end{bmatrix} \quad V = \begin{bmatrix} V_1 \\ \vdots \\ V_b \end{bmatrix}$$

$$H = \begin{bmatrix} 1 & 1 & 1 & 1 & . & . & . & 1 & 0 & 0 \\ . & . & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & . & . \\ 1 & 1 & 1 & 1 & . & . & . & . & 0 & 0 \\ 1 & 1 & 1 & 0 & . & . & . & . & 0 & 0 \\ 1 & 1 & 0 & 0 & . & . & . & . & 0 & 0 \\ 1 & 0 & 0 & 0 & . & . & . & . & 0 & 0 \\ 0 & 0 & 0 & 0 & . & . & . & . & 0 & 0 \\ 0 & 0 & 0 & 0 & . & . & . & . & 0 & 0 \end{bmatrix}$$

H is a $b \times b$ matrix of rank $b-2$, T is a $b \times 1$ vector of the $b-1$ batch durations that each batch was in the MFT plus the time t since the b^{th} batch, V_f is the $b \times 1$ vector of average volumetric flowrates, V is the $b \times 1$ vector of average melter volumes, V_s is the $b \times 1$ vector of sample volumes, and M is the $b \times 1$ vector of sample masses. Let $A \cdot B = \{a_{ij} b_{ij}\}$ denote the Hadamard product of A and B. Then

$$A = \frac{1}{\rho} T \cdot M \cdot V_f \cdot V_s^{-h} \cdot V^{-h} \quad (\text{B.4.11})$$

where the exponent, $-h$, indicates the elements of the matrix have been replaced with their reciprocals: $V^{-h} = \{1/V_i\}$. Define

$$\exp(-A) = \{e^{-a_i}\}$$

Also, let w be a $b \times 6 - 1$ vector of zeros augmented on the right by a 6×1 vector whose first $6 - 1$ elements are equal to 1 and the 6th element is 0:

$$W = \left[\begin{array}{c|c} 0_{b \times b-1} & j_{b-1} \\ \hline & 0 \end{array} \right]$$

Then

$$\begin{aligned} Q_b &= [j_b - \exp(-A)] \cdot \exp[-(H+H)A] \\ &= \exp[-(H+W)A] - \exp[-(I+H+W)A] \end{aligned} \quad (B.4.12)$$

Note that Q_b is $b \times 1$. If more than one pour is made per MFT batch, the glass compositions can be predicted simultaneously. Construct an A_i vector for each pour and concatenate them side by side into a single matrix A . This matrix A can then be used in (B.4.12). Finally,

$$C_{t_b} = Q'_b C_{Mi} \quad (B.4.13)$$

Equations (B.4.12) and (B.4.13) make up the matrix version of (B.4.10).

The multiple constituent form of (B.4.13) is given by

$$C_{t_{bc}} = (I_k \otimes Q'_b) M_{Mc} \quad (B.4.14)$$

where M_{Mc} as before contains the C_{Mi} stacked on top of each other. $C_{t_{bc}}$ is a $k \times 1$ vector of the C_{t_b} of the 'k' constituents after b batches. If C_{Mi} and M_{Mc} are in units of mass of constituent per volume of feed, then they must be multiplied by the ratio of the glass density to the feed density: ρ_g/ρ_f .

B.4.3 Estimating the Melter Composition

Equation (B.4.14) is estimated by replacing M_{Mc} with its estimate $\hat{M}_{Mc}$ given by (B.3.5) or (B.3.16) and replacing Q_b with its estimate $\hat{Q}_b$. The calculation of $\hat{Q}_b$ is given below. However, in order to calculate the covariance matrix of the estimate of C_{tbc} , it is necessary to rewrite (B.4.14) as

$$\hat{C}_{tbc} = (I_k \otimes j'_b) [(j_k \otimes \hat{Q}_b) \cdot \hat{M}_{Mc}] \quad (B.4.15)$$

Let $\Sigma_{C_t}^A$ denote the covariance matrix of (B.4.15). The derivation of $\Sigma_{C_t}^A$ is accomplished using some results based on the Hadamard product which are not commonly found in the literature. Therefore, a more detailed explanation is necessary. $\Sigma_{C_t}^A$ is a function of $\Sigma_{\hat{Q}}$ and $\Sigma_{\hat{M}_{Mc}}$ where $\Sigma_{\hat{M}_{Mc}}$ is given by (B.3.6) or (B.3.17), depending upon whether (B.3.5) or (B.3.16) is used to estimate M_{Mc} . The estimate of $\Sigma_{C_k}^A$ is

$$\Sigma_{C_t}^A = (I_k \otimes j'_b) \Sigma_{QM}^A (I_k \otimes j_b) \quad (B.4.16)$$

where Σ_{QM}^A is the covariance matrix of $(j_k \otimes \hat{Q}_b) \cdot \hat{M}_{Mc}$. If M_{Mc} is multiplied by ρ_g/ρ_f then Σ_{QM}^A must be multiplied by ρ_g^2/ρ_f^2 .

$$\begin{aligned} \Sigma_{QM}^A &= E [(j_k \otimes \hat{Q}_b) \cdot \hat{M}_{Mc} (j'_k \otimes \hat{Q}'_b) \cdot \hat{M}'_{Mc}] - E[(j_k \otimes \hat{Q}_b) \cdot \hat{M}_{Mc}] E[(j'_k \otimes \hat{Q}'_b) \cdot \hat{M}'_{Mc}] \\ &= E [(j_k \otimes \hat{Q}_b)(j_k \otimes \hat{Q}'_b) \cdot \hat{M}_{Mc} \hat{M}'_{Mc}] - E(j_k \otimes \hat{Q}_b) E(j'_k \otimes \hat{Q}'_b) \cdot E(\hat{M}_{Mc}) E(\hat{M}'_{Mc}) \\ &= [(j_k j'_k) \otimes (\Sigma_{\hat{Q}_b} + Q_b Q'_b)] \cdot (\Sigma_{\hat{M}_{Mc}} + M_{Mc} M'_{Mc}) - [(j_k j'_k) \otimes (Q_b Q'_b)] \cdot (M_{Mc} M'_{Mc}) \\ &= [(j_k j'_k) \otimes \Sigma_{\hat{Q}_b}] \cdot \Sigma_{\hat{M}_{Mc}} + [(j_k j'_k) \otimes \Sigma_{\hat{Q}_b}] \cdot (M_{Mc} M'_{Mc}) \\ &\quad + \Sigma_{\hat{M}_{Mc}} \cdot [(j_k j'_k) \otimes (Q_b Q'_b)] \end{aligned} \quad (B.4.17)$$

where $E(A)$ denotes the average value of A if A is estimated n times from n samples and n is allowed to approach infinity. Equation (B.4.17) denotes the true variance covariance matrix, Σ_{QM} . Note that the covariance structure involves covariance matrices and the true but unknown vectors Q_b and M_{Mc} . Because Q_b and M_{Mc} are also found in (B.4.17) and must be estimated, (B.4.17) cannot be estimated by direct substitution. The estimate of (B.4.17) is given by

$$\begin{aligned} \hat{\Sigma}_{QM} = & \left[(j_k j'_k) \otimes (\hat{Q}_b \hat{Q}'_b) \right] \cdot (\hat{M}_{Mc} \hat{M}'_{Mc}) \\ & - \left[(j_k j'_k) \otimes \left((\hat{Q}_b \hat{Q}'_b) - \hat{\Sigma}_{Qb} \right) \right] \cdot \left[(\hat{M}_{Mc} \hat{M}'_{Mc}) - \hat{\Sigma}_{M_{Mc}} \right] \end{aligned} \quad (B.4.18)$$

In order to calculate (B.4.18) Σ_{Qb} must be obtained.

B.4.3.1 Estimation of Q_b and Σ_{Qb}

The only part of Q_b that will involve measurements is A . It is assumed that the elements of T are known and that the elements of M , V_f , V , and V_s are positive and symmetrically distributed about their corresponding means. Also, it is assumed that M , V_f , V , and V_s are uncorrelated with one another. Since (B.4.11) is a function of the reciprocals of the elements of V and V_s , an unbiased estimator does not exist. However, if multiple measurements of V and V_s can be made per batch and multiple samples analyzed then a consistent estimator of A can be obtained by using the batch averages as the elements in M , V_f , V and V_s . (A consistent estimator is a biased estimator where the bias shrinks to zero as the sample size increases.) Also, multiple measurements will permit the estimation of the corresponding covariance matrices.

Since Q_b is a nonlinear function of A , Σ_{Qb} must be approximated:

$$\hat{\Sigma}_{Qb} = \left[\frac{\partial Q_b}{\partial A'} \right] \hat{\Sigma}_A \left[\frac{\partial Q_b'}{\partial A'} \right] \quad (B.4.19)$$

where $\Sigma_{\hat{A}}$ denotes the covariance matrix of $\hat{A}$ and the estimate of A is based on the batch means of M , V_f , V , and V_s . Also, A in (B.4.19) is 6×1 . If more than one pour per batch is made, then it is possible to calculate an over $\Sigma_{\hat{A}}$, but it is computationally easier to estimate $\Sigma_{\hat{A}}$ for each pour separately. This will save computer resources.

$$\begin{aligned} \frac{\partial Q_b}{\partial A'} = & - (H+W) \cdot \left\{ [\exp[-(H+W)A]] \otimes j'_b \right\} \\ & + (I+H+W) \cdot \left\{ [\exp[-(I+H+W)A]] \otimes j'_b \right\} \end{aligned} \quad (B.4.20)$$

Equation (B.4.20) is evaluated at $\hat{A}$. Equation (B.4.19) is based on the first term of a Taylor series expansion of Q_b (see Appendix F).

Using the same method used to derive (B.4.17), it is seen that

$$\begin{aligned} \Sigma_A = & \frac{1}{\rho^2} TT' \cdot \left[\left(\Sigma_M - \mu_M \mu'_M \right) \cdot \left(\Sigma_{V_f} - \mu_{V_f} \mu'_{V_f} \right) \cdot \left(\Sigma_{V^{-h}} - \mu_{V^{-h}} \mu'_{V^{-h}} \right) \cdot \left(\Sigma_{V_s^{-h}} - \mu_{V_s^{-h}} \mu'_{V_s^{-h}} \right) \right. \\ & \left. - \left(\mu_M \mu'_M \right) \cdot \left(\mu_{V_f} \mu'_{V_f} \right) \cdot \left(\mu_{V^{-h}} \mu'_{V^{-h}} \right) \cdot \left(\mu_{V_s^{-h}} \mu'_{V_s^{-h}} \right) \right] \end{aligned} \quad (B.4.21)$$

where μ denotes the $b \times 1$ vector of true values for the corresponding subscript. $\Sigma_{V^{-h}}$ and $\Sigma_{V_s^{-h}}$ must also be approximated:

$$\Sigma_{V^{-h}} \cong [(V \cdot V)^{-h} (V' \cdot V')^{-h}] \cdot \Sigma_V$$

and

$$\Sigma_{V_s^{-h}} \cong [(V_s \cdot V_s)^{-h} (V'_s \cdot V'_s)^{-h}] \cdot \Sigma_{V_s} \quad (B.4.22)$$

Approximations (B.4.22) can be estimated by direct substitution. However, (B.4.21), like (B.4.17), cannot be estimated by direct substitution. Since (B.4.22) are approximations, the estimate of (B.4.21) will also be approximate. An estimate of Σ_A is

$$\Sigma_A = \frac{1}{\rho^2} TT' \cdot \left[\overline{MM'} \cdot \left(\overline{V_f V_f'} \right) \cdot \left(\overline{V_s}^{-h} \overline{V_s}^{-h'} \right) \cdot \left(\overline{V}^{-h} \overline{V}^{-h'} \right) \right. \\ \left. - \left(\overline{MM'} - \hat{\Sigma}_M \right) \cdot \left(\overline{V_f V_f'} - \hat{\Sigma}_{V_f} \right) \cdot \left(\overline{V}^{-h} \overline{V}^{-h'} - \hat{\Sigma}_V^{-h} \right) \cdot \left(\overline{V_s}^{-h} \overline{V_s}^{-h'} - \hat{\Sigma}_{V_s}^{-h} \right) \right] \quad (B.4.23)$$

where the $\hat{\Sigma}$'s denote the estimated covariance matrices of the averages and the bar above M, V, V_f , and V_s indicate they are averages of n measurements. Estimates of (B.4.22) would be used in (B.4.23). Equation (B.4.19) would be estimated using Equations (B.4.20) and (B.4.23), and (B.4.19) would be used in (B.4.18). Finally (B.4.18) would be substituted into (B.4.16) and $\Sigma_{\hat{C}_t}$ would be estimated.

Proofs of the methods used to obtain Equations (B.4.19) to (B.4.23) are given in Appendix F. As in the case of the combined MFT estimate, the concentration estimates along with the variances and covariances corresponding to the i^{th} pour during the b^{th} batch can be extracted from (B.4.14) and (B.4.16) and used to construct Hotelling T^2 statistics and confidence intervals. The degrees of freedom for these statistics are unknown, but it is assumed that they are greater than or equal to the degrees of freedom of the variable with the fewest observations. Also, a control scheme for the differences between the predicted glass composition and the observed composition could be constructed. Estimators similar to those given in (B.3.16) and (B.3.17) would be used to combine the predicted glass compositions given in (B.4.14) with the observed compositions.

B.5 CONCLUSIONS AND RECOMMENDATIONS

An important part of waste form qualification is the demonstration of a stable vitrification process. If something in the process were to go awry, there must be a mechanism for detecting such changes in the process that may

have an adverse effect on product quality. Statistical process control is such a mechanism. The correlation structure between both batches and constituents in the product makes the statistical process control for the LFCM process unique. Several multivariate process control schemes have been developed for the FPT, MFT, and melter as outlined below.

FPT

- Monitor the measured FPT composition allowing for some batch variation.
- Monitor the measured FPT composition without allowing for any batch variation.

FMFT

- Monitor the measured MFT composition allowing for some batch variation.
- Monitor the measured MFT composition without allowing for any batch variation.
- Monitor the difference between the measured MFT composition and the FPT-based estimate of MFT composition.
- Monitor the combined FPT-based and measured MFT composition.

Melter

- Monitor the measured glass composition allowing for batch variation.
- Monitor the measured glass composition without allowing for batch variation.
- Monitor the difference between the measured glass composition and the predicted composition based on FPT and MFT measurements and the mass balance model.
- Monitor the estimated glass composition derived from combining the measured glass estimate with the predicted estimate from FPT/MFT measurements and the mass balance model.

The choice of which of the above process control schemes should be implemented in the LFCM is dependent upon the objectives and sensitivities of each scheme. It is recommended that such sensitivities be studied further through application of the various control schemes to simulated data.

These control schemes are based on Hotelling's T^2 statistic. The Hotelling T^2 statistics require the estimation of the variance-covariance matrices along with the estimation of the batch compositions. In order to get good estimates of the covariance matrices, larger sample sizes than those needed for the one-constituent-at-a-time approach are needed. The required number of batches, samples per batch, and analyses per sample to obtain estimates of the covariance matrices have been presented.

Further research is needed to determine how to calculate the degrees of freedom of the Hotelling T^2 statistics for the melter, FPT, and MFT control schemes involving Σ_B . The assumed value of $b-1$ can be used but more accurate estimates would increase the sensitivity of the control schemes.

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APPENDIX C

MULTIVARIATE REGRESSION USING THE GENERAL LINEAR MODEL

APPENDIX C

MULTIVARIATE REGRESSION USING THE GENERAL LINEAR MODEL

The standard form of the multivariate regression model presented in most texts is

$$Y = XB + E \quad (C.1)$$

where Y is $n \times p$, X is the $n \times k$ matrix of regressors, B is the $k \times p$ matrix of parameters and E is the $n \times p$ matrix of errors. The covariance structure of E is described as follows. The variance-covariance matrix of a row of E is Σ and the covariance between columns is $\sigma_{ij} I$ where σ_{ij} is the ij^{th} element of Σ . (See for example Johnson and Wickiarn 1982.) The columns of E are correlated but the rows are independent. The uniformly minimum variance unbiased estimator of B is

$$\hat{B} = (X'X)^{-1} X'Y \quad (C.2)$$

The covariance of $\hat{B}$ is $\Sigma \otimes (X'X)^{-1}$ where $A \otimes B$ denotes the Kronecker or direct matrix product of A and B (see Appendix D). Usually (C.2) is given in pieces:

$$\text{Cov}(\hat{b}_i, \hat{b}_j) = \sigma_{ij} (X'X)^{-1} \quad (C.3)$$

A more convenient form of the multivariate regression model employs the general linear regression model. This is formed by applying the vec operator to (C.1). Let

$$Y_C = \text{vec}(Y) = \begin{bmatrix} Y_{11} \\ \vdots \\ Y_{n1} \\ Y_{12} \\ \vdots \\ Y_{n2} \\ \vdots \\ Y_{1p} \\ \vdots \\ Y_{np} \end{bmatrix}$$

Y_C is $np \times 1$ and is a column vector composed of the columns of Y stacked on top of each other. Similarly Let $B_C = \text{vec}(\hat{B})$ and $E_C = \text{vec}(E)$. Also, let $Z = I_p \otimes X$. Now (C.1) can be rewritten as

$$Y_C = Z B_C + E_C \quad (C.4)$$

Where $\text{cov}(E_C) = \Sigma \otimes I_n$ which is the same covariance structure as defined for (C.1) except it can be obtained from (C.4) without defining it in pieces. Equation (C.4) is the univariate form of (C.1). As will be shown, the estimator of B_C is equal to $\text{vec}(\hat{B})$. Both Equations (C.1) and (C.4) account for the covariance structure of E . However, (C.4) is much more easily adapted to more general assumptions about the covariance structure of the data which is needed for this report.

The uniformly minimum variance unbiased estimator of B_C is

$$\hat{B}_C = (Z'Z)^{-1} Z'Y_C \quad (C.5)$$

The covariance matrix for $\hat{B}_C$ is

$$\text{Var}(\hat{B}_C) = \Sigma \otimes (X'X)^{-1} \quad (C.6)$$

Equation (C.6) can be derived directly from (C.5). Note that

$$\begin{aligned} \hat{B}_C &= (Z'Z)^{-1} Z'Z B + (Z'Z)^{-1} Z'E \\ &= B_C + (Z'Z)^{-1} Z'E_C \\ \text{Cov}(\hat{B}_C) &= E(\hat{B}_C - B_C)(\hat{B}_C' - B_C') \\ &= E(Z'Z)^{-1} Z' E_C E_C' Z(Z'Z)^{-1} \\ &= (Z'Z)^{-1} Z' (\Sigma \otimes I_n) Z(Z'Z)^{-1} \\ &= [(I_p \otimes X')(I_p \otimes X)]^{-1} (I_p \otimes X') (\Sigma \otimes I_n) (I_p \otimes X) [(I_p \otimes X')(I_p \otimes X)]^{-1} \\ &= [I_p \otimes (X'X)^{-1}] (\Sigma \otimes X'X) [I_p \otimes (X'X)^{-1}] \\ &= \Sigma \otimes (X'X)^{-1} \end{aligned}$$

where $(A \otimes B)(C \otimes D) = AC \otimes BD$ provided AC and BD exist and $(A \otimes B)^{-1} = A^{-1} \otimes B^{-1}$ provided A^{-1} and B^{-1} exist.

Since $\text{Var}(E_C) \neq \sigma^2 I$ it might seem that

$$\hat{B}_C = [Z'(\Sigma^{-1} \otimes I) Z]^{-1} Z'(\Sigma^{-1} \otimes I) Y_C \quad (C.7)$$

is the uniformly minimum variance unbiased estimator. It turns out that under the assumptions of the standard multivariate regression model (i.e., $\text{Var}(E_c) = \Sigma \otimes I$) (C.5) and (C.7) are equivalent. Expanding (C.7) we get

$$\begin{aligned}
 B_c &= [(I_p \otimes X')(\Sigma^{-1} \otimes I_n)(I_p \otimes X)]^{-1} (I_p \otimes X')(\Sigma^{-1} \otimes I_n) y_c \\
 &= (\Sigma^{-1} \otimes X'X)^{-1} (\Sigma^{-1} \otimes X') y_c \\
 &= [\Sigma \otimes (X'X)^{-1}] (\Sigma^{-1} \otimes X') y_c \\
 &= [I_p \otimes (X'X)^{-1}X'] y_c \\
 &= \text{vec}(\hat{B})
 \end{aligned} \tag{C.8}$$

APPENDIX D

THREE MATRIX PRODUCTS

APPENDIX D

THREE MATRIX PRODUCTS

Three different matrix products are used in this report. The products are the regular, Hadamard and Kronecker products.

REGULAR MATRIX PRODUCT

The matrix product most commonly used in matrix algebra is the regular matrix product. Let A be an $m \times n$ matrix and B be an $n \times p$ matrix. This product is denoted by writing ' AB '. It is the inner product of the rows of A with the columns of B . Therefore, the number of columns of A must be equal to the number of rows of B . If $m \neq p$ then BA is not defined.

Properties

1. Not commutative

If $m = p$, it is not always true that $AB = BA$.

2. Associative

$$(AB)C = A(BC)$$

3. Distributive over addition

A. From the left provided the regular products are defined

$$A(B + C) = AB + AC$$

B. From the right provided the regular products are defined

$$(B + C)A = BA + CA$$

4. Transpose

$$(AB)' = B'A'$$

5. Inverse

$$(AB)^{-1} = B^{-1}A^{-1} \text{ provided } A^{-1} \text{ and } B^{-1} \text{ exist.}$$

HADAMARD PRODUCT

Let A be an $m \times n$ matrix and B be an $p \times q$ matrix. Then the Hadamard product is denoted in this report by $A \cdot B$ and is the element wise product of A and B. In other words the ij^{th} element of $A \cdot B$ is the product of the ij^{th} elements of A and B. Hence, this product is only defined for matrices with the same dimensions. Since the Hadamard product is the element wise product of the elements of A and B, it has all the properties that multiplication of scalars enjoy.

KRONECKER OR DIRECT PRODUCT

Let A be an $m \times n$ matrix and B be a $p \times q$ matrix. The Kronecker product produces an $mp \times nq$ matrix and is written $A \times B$.

$$A \times B = \begin{matrix} & a_{11}B & . & . & . & a_{1n}B \\ & . & . & . & . & . \\ & . & . & . & . & . \\ & . & . & . & . & . \\ a_{m1}B & . & . & . & . & A_{mn}B \end{matrix}$$

B is multiplied by each element of A and then the resulting mn matrices, $a_{ij}B$ $i = 1, \dots, m$; $j = 1, \dots, n$; are arranged in an array.

Properties

1. Not commutative

$$A \times B \neq B \times A$$

2. Associative

$$A \times (B \times C) = (A \times B) \times C$$

3. Distributive over addition

$$A. \quad A \times (B + C) = A \times B + A \times C$$

$$B. \quad (B + C) \times A = B \times A + C \times A$$

4. Transpose

$$(A \times B)' = A' \times B'$$

5. Inverse

$$(A \times B)^{-1} = A^{-1} \times B^{-1} \text{ provided } A^{-1} \text{ and } B^{-1} \text{ exist}$$

6. Product of Kronecker Products

$$(A \times B) (C \times D) = AC \times BD \text{ provided } AC \text{ and } BD \text{ products are defined.}$$

APPENDIX E

ANALYSIS OF VARIANCE MODELS

APPENDIX E

The analysis of variance models used in this report are random two-fold nested models. For the h^{th} constituent, the model is

$$Y_{hijk} = \mu_h + B_i + S_{j(i)} + A_{k(i,j)} \quad (E.1)$$

where μ_h is the true overall average concentration of the h^{th} constituent, B_i is the effect of the i^{th} batch, $S_{j(i)}$ is the effect of the j^{th} sample from the i^{th} batch and $A_{k(i,j)}$ is the k^{th} analysis on the j^{th} sample from the i^{th} batch. The effects B_i , $S_{j(i)}$ and $A_{k(i,j)}$ are assumed to be independently distributed with zero means and variances σ_{Bh}^2 , σ_{Sh}^2 and σ_{Ah}^2 . The expected value and variance-covariance structure for the h^{th} constituent are

$$E(y_{hijk}) = \mu_h \quad (E.2)$$

and

$$\begin{aligned} \text{Cof}(y_{hijk}, y_{hi'j'k'}) &= \sigma_{Bh}^2 + \sigma_{Sh}^2 + \sigma_{Ah}^2 & i=i', j=j', k=k' \\ &= \sigma_{Bh}^2 + \sigma_{Sh}^2 & i=i', j=j', k \neq k' \\ &= \sigma_{Bh}^2 & i=i', j \neq j' \\ &= 0 & i \neq i' \end{aligned} \quad (E.3)$$

Assume that there are 'b' batches, 's' samples per batch and 'a' analyses per sample. Then the matrix form of (E.3) is

$$\Sigma_{hh} = \sigma_{Bh}^2 (I_b \otimes J_s \otimes J_a) + \sigma_{Sh}^2 (I_b \otimes I_s \otimes J_a) + \sigma_{Ah}^2 (I_b \otimes I_s \otimes I_a) \quad (E.4)$$

where J_s and J_a are $s \times s$ and $a \times a$ matrices of ones (Hocking 1985).

Equation (E.4) holds for all h . Let the covariance between the h and h' constituents by $\sigma_{Bhh'}$, $\sigma_{Shh'}$ and $\sigma_{Ahh'}$ due to the effects of B_i , $S_{j(i)}$ and $A_{k(ij)}$ respectively. Then

$$\begin{aligned} \text{Cov}(y_{hijk}, y_{h'i'j'k'}) &= \sigma_{Bhh'} + \sigma_{Ahh'} & h \neq h', i=i', j=j', k=k' \\ &= \sigma_{Bhh'} + \sigma_{Shh'} & h \neq h', i=i', j=j', k \neq k' \\ &= \sigma_{Bhh'} & h \neq h', i=i', j \neq j' \\ &= 0 & h \neq h', i \neq i' \end{aligned} \quad (E.5)$$

If $h=h'$ then (E.5) is given by (E.3). In matrix form (E.5) is

$$\begin{aligned} \Sigma_{hh'} &= \sigma_{Bhh'}(I_b \otimes J_s \otimes J_a) + \sigma_{Shh'}(I_b \otimes I_s \otimes J_a) \\ &\quad + \sigma_{Ahh'}(I_b \otimes I_s \otimes I_a) \end{aligned} \quad (E.6)$$

Let $h=1, \dots, k$. Combining (E.4) and (E.6) for all the constituents gives the covariance matrix of all the y 's:

$$\Sigma_y = \Sigma_B \otimes I_b \otimes J_s \otimes J_a + \Sigma_S \otimes I_b \otimes I_s \otimes J_a + \Sigma_A \otimes I_b \otimes I_s \otimes I_a \quad (E.7)$$

where Σ_B , Σ_S and Σ_A are the covariance matrices of the k constituents due the batch, sampling, and analytical effects respectively. Equation (E.7) is the underlying covariance matrix of the C_{NC} in the FPT and provides the basis for the rest of the estimates used in this report.

APPENDIX F

STATISTICAL METHODS

APPENDIX F

The statistical methods used to determine the variance-covariance matrices for the predicted melter composition are not common to the statistical literature. Therefore, they are proven here. The results given below fall into four main categories: outer products of Hadamard products of vectors, Taylor series expansion of functions that operate on the elements of a matrix, multivariate extensions of Lehman (1983) theorems giving approximations to the expected value and variance of nonlinear functions of random variables, and a multivariate extension of Goodman's (1962) variance formulae for products of random variables.

F.1 OUTER PRODUCT OF HADAMARD PRODUCTS OF VECTORS

Theorem F1

Let x_i $i=1, \dots, k$ be $m \times 1$ vectors and let y_i $i=1, \dots, k$ be $n \times 1$ vectors.

Let $p = x_1 \cdot x_2 \cdot \dots \cdot x_k = \prod_{i=1}^k x_i$ be the Hadamard product of the x_i $i=1, \dots, k$ and

let $q = y_1 \cdot y_2 \cdot \dots \cdot y_k = \prod_{i=1}^k y_i$ be the Hadamard product of the y_i $i=1, \dots, k$.

Then $pq' = \prod_{i=1}^k y_i x_i'$, and $qp' = \prod_{i=1}^k y_i x_i'$, where pq' is $m \times n$ and qp' is $n \times m$.

Proof

$$pq' = \prod_{i=1}^k x_i \prod_{i=1}^k y_i$$

The $h\ell$ th element of pq' is $\prod_{i=1}^k x_{ih} \prod_{i=1}^k y_{i\ell} = \prod_{i=1}^k x_{ih} y_{i\ell}$

The right hand side of the equality is the $h\ell$ th element of $\prod_{i=1}^k x_i y_i'$

Since the Hadamard product is the element wise multiplication of two or more matrices, the transpose of a Hadamard product is equal to the Hadamard product of the transposed matrices, and this completes the proof.

Note that the reason why this theorem holds is because the only arithmetic operator used on the elements of the matrices is multiplication which is cumulative and associative. If the x_i and y_i are $m \times n$ matrices where both m and n are greater than one or if the inner product of p and q , $p'q$ is used, then this theorem does not hold because the sum of products is not equal to the product of sums.

F.2 EXPECTED VALUE AND COVARIANCE MATRIX OF A VECTOR VALUED NONLINEAR FUNCTION OF A VECTOR

Eric Lehman (1983) proved a theorem that gives approximations for the expected value and variance of a nonlinear function of a random variable. He also extended the theorem to include a scalar valued function of a vector. The result needed for this report is a very simple extension of Lehman's (1983) theorems, and as will be seen can be viewed as a direct application of these theorems to vector valued functions while linear algebra is used to keep track of the details.

Scalar Valued Function of a Scalar

(See Theorem 5.1 in Section 2.5 of Lehman 1983):

Let X_i $i = 1, \dots, n$ be a random sample from a population with some distribution. The distribution has the following properties: $E(X_i) = \mu$, $\text{Var}(X_i) = \sigma^2$ $i = 1, \dots, n$ and $\mu < \infty$, $\sigma^2 < \infty$, and $E(X_i^4) < \infty$ $i = 1, \dots, n$. Let $\bar{X}$ be the arithmetic average of the X_i with variance σ^2/n . Let $f(\bar{X})$ be some function of $\bar{X}$ with the following properties: the first four derivatives of f exist and are bounded for all $\bar{X} \in I$ where $\text{Prob}(\bar{X} \in I) = 1$. Then

$$E[f(\bar{X})] = f(\mu) + \frac{\sigma^2}{2n} f''(\mu) + R_n \quad (\text{F.1})$$

Also, if the fourth derivative of f^2 is bounded then

$$\text{Var} [f(\bar{X})] = \frac{\sigma^2}{n} [f'(\mu)]^2 + R_n \quad (\text{F.2})$$

where in both cases R_n is $O(1/n^2)$: and n_0 exists such that the sequence $R_n(\mu) < A/n^2$ for $n > n_0$ and $A < \infty$.

See Lehman (1983) for the proof.

Scalar Valued Function of a Vector

[See bottom of page 110 and Problem 5.26 of Chapter 2 in Lehman (1983).]

As an exercise for the reader, Lehman (1983) extends the above theorem to the case in which $\bar{X}$ is a vector of averages and $f(\bar{X})$ is still a scalar. Let $\bar{X}$ denote the vector of k averages. Let $\underline{\mu}$ denote expected value of $\bar{X}$ and $\frac{1}{n} \Sigma$ denote the covariance matrix of $\bar{X}$.

Lehman proves his result using the regular Taylor series expansion of a function of several variables. However, it is more convenient to use the matrix notation of Gallant (1987). In Gallant's notation

$$f(\bar{X}) = f(\underline{\mu}) + \left[\frac{\partial f(\bar{X})}{\partial \bar{X}'} \right]_{\bar{X}=\underline{\mu}} (\bar{X} - \underline{\mu}) + \frac{1}{2} (\bar{X} - \underline{\mu})' \left[\frac{\partial^2 f(\bar{X})}{\partial \bar{X} \partial \bar{X}'} \right]_{\bar{X}=\underline{\mu}} (\bar{X} - \underline{\mu}) + R_n \quad (\text{F.3})$$

Gallant absorbs the third term into R_n by calculating a $\underline{\mu}^*$ such that when the second derivative of $f(\bar{X})$ is evaluated at $\underline{\mu}^*$, $R_n = 0$. $\partial^2 f(\bar{X}) / (\partial \bar{X} \partial \bar{X}')$ is called the Hessian matrix of $f(\bar{X})$, and it is symmetric if the second order derivatives of f are continuous (Gallant 1987). Let H denote this Hessian matrix.

Using (F.3), Equations (F.1) and (F.2) can be rewritten

$$E [f(\bar{X})] = f(\underline{\mu}) + \frac{1}{2n} E [(\bar{X} - \underline{\mu})' H (\bar{X} - \underline{\mu})] + R_n \quad (\text{F.4})$$

$$= f(\underline{\mu}) + \frac{1}{2n} \text{trace} (H \Sigma) + R_n \quad (\text{F.5})$$

and

$$\text{Var}[f(\bar{X})] = \frac{1}{n} J \Sigma J' + R_n \quad (\text{F.6})$$

where

$$J = \left. \frac{\partial}{\partial \bar{X}'} f(\bar{X}) \right|_{\bar{X}=\mu} \quad \text{and } J \text{ is } 1 \times K.$$

Equation (F.5) holds if H is symmetric. The proof that $E[(\bar{X}-\mu)'H(\bar{X}-\mu)] = \text{trace}(H\Sigma)$ is given in Hocking (1985) for Corollary 2.2.1. If H is not symmetric, then (F.4) holds.

The matrix form of R_n is complicated but will be equivalent to the rest of the Taylor series in several variables. Therefore, R_n is $O(1/n^2)$ (Lehman 1983).

Vector Valued Function of a Vector

Let $f(\bar{X})$ now denote a $q \times 1$ vector which is a function of the $k \times 1$ vector. Then $f(\bar{X})$ can be written as

$$f(\bar{X}) = \begin{bmatrix} f_1(\bar{X}) \\ \vdots \\ f_q(\bar{X}) \end{bmatrix} \quad (\text{F.7})$$

where each of the f_i $i=1, \dots, q$ is a scalar valued function of a vector. The Taylor series of $f(\bar{X})$ is

$$\begin{aligned} f(\bar{X}) &= f(\mu) + \left. \frac{\partial}{\partial \bar{X}'} f(\bar{X}) \right|_{\bar{X}=\mu} (\bar{X}-\mu) + \frac{1}{2} [I_q \times (\bar{X}-\mu)'] \frac{\partial^2 f(\bar{X})}{\partial \bar{X} \partial \bar{X}'} (\bar{X}-\mu) + R_n \\ &= C_q[f_i(\mu)] + C_q[J_i(\bar{X}-\mu)] + \frac{1}{2} C_q[(\bar{X}-\mu)'H_i(\bar{X}-\mu)] + R_n \end{aligned}$$

where J_i and H_i are the Jacobian and Hessian matrices of each f_i $i=1, \dots, q$, and $C_q(A_i)$ denotes a block column vector of the matrices A_i .

The expected value and covariance matrices of $f(\bar{X})$ are now easily seen to be

$$E[f(\bar{X})] = f(\underline{\mu}) + \frac{1}{2n} C_q [E (\bar{X} - \underline{\mu})' H_i (\bar{X} - \underline{\mu})] + R_n \quad (F.7)$$

$$= f(\underline{\mu}) + \frac{1}{2n} C_q [\text{trace}(H_i \Sigma)] + R_n \quad (F.8)$$

and

$$\text{Var}[f(\bar{X})] = \frac{1}{n} \left(\frac{\partial}{\partial \bar{X}'} f(\bar{X}) \right) \Sigma \left(\frac{\partial}{\partial \bar{X}} f(\bar{X})' \right) \bigg|_{\bar{X}=\underline{\mu}} \quad (F.9)$$

Equation (F.8) holds if all the H_i are symmetric. Equation (F.9) holds if the first four derivatives of the f_i^2 are bounded.

These results are not true for $f_i(X) = X^P$ $P < 1$ unless the interval containing X is strictly bounded away from zero (Lehman 1983).

F.3 VARIANCE-COVARIANCE MATRIX OF HADAMARD PRODUCTS OF RANDOM VECTORS

The result given here is a multivariate extension of a result due to Goodman (1960, 1962). Goodman (1962) derived exact variance formulas for the products of random variables. Let $X_1, \dots, X_p$ be random variables that are mutually independent with $E(X_i) = \mu_i$ and $\text{Var}(X_i) = \sigma_i^2$. Then

$$\text{Var} \left(\prod_{i=1}^p X_i \right) = \prod_{i=1}^p (\sigma_i^2 + \mu_i^2) - \prod_{i=1}^p \mu_i^2 \quad (F.10)$$

(Goodman 1962). If the X_i $i=1, \dots, p$ are randomly sampled n_i times

respectively and the product $\prod_{i=1}^p \bar{X}_i$ is calculated, then (F.10) becomes

$$\text{Var} \left(\sum_{i=1}^p \bar{X}_i \right) = \sum_{i=1}^p \left(\frac{\sigma_i^2}{n_i} + \mu_i^2 \right) - \sum_{i=1}^p \mu_i^2 \quad (\text{F.11})$$

Goodman (1962) found that (F.10) and (F.11) cannot be unbiasedly estimated by directly substituting in unbiased estimates for the σ_i^2 and μ_i . Instead he found that unbiased estimates of (F.10) and (F.11) are respectively given by

$$\hat{\text{Var}} \left(\sum_{i=1}^p \bar{X}_i \right) = \sum_{i=1}^p \omega_i - \sum_{i=1}^p h_i \quad (\text{F.12})$$

and

$$\hat{\text{Var}} \left(\sum_{i=1}^p \bar{X}_i^2 \right) = \sum_{i=1}^p \bar{X}_i^2 - \sum_{i=1}^p h_i \quad (\text{F.13})$$

where

$$\omega_i = \sum_{k=1}^{n_i} \bar{X}_{ik}^2 / n_i$$

and

$$h_i = \bar{X}_i^2 - \sum_{k=1}^{n_i} (X_{ik} - \bar{X}_i)^2 / [n_i(n_i - 1)]$$

The purpose here is to extend Goodman's results to Hadamard products of the X_i where now the X_i are $m \times 1$ vectors, and more specifically, $m \times 1$ vectors of m sample means. Goodman (1960, 1962) also considered the case where the X_i are correlated. However, only the case of independent vectors X_i will be considered here.

Theorem F3

Let X_i $i=1, \dots, p$ be $m \times 1$ vectors which are mutually independent. Also, let $E(X_i) = \mu_i$ and $\text{Var}(X_i) = \Sigma_i$. Let

$$\prod_{i=1}^p X_i$$

be the Hadamard product of the p vectors. Then

$$\text{Var} \left(\prod_{i=1}^p X_i \right) = \prod_{i=1}^p (\Sigma_i + \mu_i \mu_i') - \prod_{i=1}^p \mu_i \mu_i' \quad (\text{F.14})$$

and if each of the X_i are randomly observed n_i times and $\bar{X}_i$ calculated where $\bar{X}_i$ an $m \times 1$ vector of the $\bar{X}_{ij}$ for $i=1, \dots, p$ and $j=1, \dots, m$ then

$$\text{Var} \left(\prod_{i=1}^p \bar{X}_i \right) = \prod_{i=1}^p \left(\frac{\Sigma_i}{n_i} + \mu_i \mu_i' \right) - \prod_{i=1}^p \mu_i \mu_i' \quad (\text{F.15})$$

Proof

Let $r = \prod_{i=1}^p X_i$. Then

$$\begin{aligned} \text{Var}(r) &= E(rr') - E(r) E(r') \\ &= E \left(\prod_{i=1}^p X_i \prod_{i=1}^p X_i' \right) - E \left(\prod_{i=1}^p X_i \right) E \left(\prod_{i=1}^p X_i' \right) \end{aligned}$$

Applying theorem F1 and carrying the expected value operator through the products

$$\begin{aligned} \text{Var}(r) &= \prod_{i=1}^p E(X_i X_i') - \prod_{i=1}^p \mu_i \mu_i' \\ &= \prod_{i=1}^p (\Sigma_i + \mu_i \mu_i') - \prod_{i=1}^p \mu_i \mu_i' \end{aligned}$$

Equation (F.15) is proven the same way noting the $E(\bar{X}_i \bar{X}_i') = 1/n_i \Sigma_i + \mu_i \mu_i'$ and the proof is complete.

To estimate Equation (F.14) and (F.15) define matrices

$$W_i = \frac{1}{n_i} \sum_{k=1}^{n_i} X_{ik} X_{ik}'$$

and

$$H_i = \bar{X}_i \bar{X}_i' - S_i/n_i$$

where the X_{ik} $k=1, \dots, n_i$ are the n_i random observations of the random vector X_i $i=1, \dots, p$.

$$\bar{X}_i = \frac{1}{n_i} \sum_{k=1}^{n_i} X_{ik}$$

$$S_i = \sum_{k=1}^{n_i} (X_{ik} - \bar{X}_i)(X_{ik} - \bar{X}_i)' / (n_i - 1)$$

Then the estimate of (F.14) is

$$\hat{\text{Var}} \left(\frac{1}{p} \sum_{i=1}^p X_i \right) = \frac{1}{p} \sum_{i=1}^p W_i - \frac{1}{p} \sum_{i=1}^p H_i \quad (\text{F.16})$$

and

$$\hat{\text{Var}} \left(\frac{1}{p} \sum_{i=1}^p \bar{X}_i \right) = \frac{1}{p} \sum_{i=1}^p \bar{X}_i \bar{X}_i' - \frac{1}{p} \sum_{i=1}^p H_i \quad (\text{F.17})$$

Equations (F.16) and (F.17) are unbiased estimators of (F.14) and (F.15) respectively. This is seen by noting that

$$E(W_i) = \Sigma_i + \mu_i \mu_i'$$

$$E(\bar{X}_i \bar{X}_i') = \Sigma_i / n_i + \mu_i \mu_i'$$

and

$$E(H_i) = \mu_i \mu_i'$$

Equation (F.11) is the justification of Equations (4.17) and (4.21), and (F.17) is the justification of (4.23).

APPENDIX G

VARIANCE/COVARIANCE MATRICES

APPENDIX G

In order to use the statistical methods given in Appendix B, covariance matrices had to be calculated. The chemical processes and the dynamics of the LFCM cause the concentrations of the oxides to be correlated. The uncertainty and correlations in the measurements are summarized in a variance-covariance matrix. There are three variance-covariance matrices to be estimated from the data: one due to batches, one due to sampling, and one due to analyses. These variance-covariance matrices are not expected to be the same. They are estimated from the data using Helmert matrices to orthonormally partition the information in the data into estimates of the three covariance matrices.

A Helmert matrix is a square orthonormal matrix: its rows are orthonormal and its columns are orthonormal. A 3x3 Helmert matrix is

$$\begin{bmatrix} 1/3 & 1/6 & 1/2 \\ 1/3 & 1/6 & -1/2 \\ 1/3 & -2/6 & 0 \end{bmatrix}$$

A 4x4 Helmert matrix is

$$\begin{bmatrix} 1/4 & 1/12 & 1/6 & 1/2 \\ 1/4 & 1/12 & 1/6 & -1/2 \\ 1/4 & 1/12 & -2/6 & 0 \\ 1/4 & -3/12 & 0 & 0 \end{bmatrix}$$

For the purposes of partitioning sums of squares and cross-products, the constant column of the Helmert matrices was omitted because it is accounted

for by the overall average of the data which is adjusted out of the data when such partitions are formed. Thus the 3x3 Helmert matrix becomes the 3x2 modified Helmert matrix,

$$\begin{bmatrix} 1/6 & 1/2 \\ 1/6 & -1/2 \\ -2/6 & 0 \end{bmatrix}$$

Let H_b , H_s , and H_a denote the modified Helmert matrices corresponding to batches, samples and analyses: H_b has the same number of rows as there are batches, H_s has the same number of rows as there are samples per batch and H_a has the same number of rows as there are analyses per sample. Next, form the following three matrices

$$X_b = H_b \times (j_s \cdot 1/s) \times (j_a \cdot 1/a)$$

$$X_s = I_b \times H_s \times (j_a \cdot 1/a)$$

$$X_a = I_b \times I_s \times H_a$$

where I_b and I_s are $b \times b$ $s \times s$ identity matrices, respectively, and j_s and j_a are $s \times 1$ and $a \times 1$ vectors of ones, respectively; and b , s and a are used to denote the number of batches, the number of samples per batch and the number of analyses per sample.

Let all the oxide concentrations be arranged into a $bs \times 8$ matrix Y :

$$Y = [\text{SiO}_2 | \text{Na}_2\text{O} | \text{Fe}_2\text{O}_3 | \text{B}_2\text{O}_3 | \text{Al}_2\text{O}_3 | \text{K}_2\text{O} | \text{ThO}_2 | \text{FssnPrdcts}]$$

The sums of squares and cross-products matrices due to batches, samples and analyses are calculated as follows.

$$R_b = X_b'Y$$

$$R_s = X_s'Y$$

$$R_a = X_a'Y$$

where ' denotes the transpose of the corresponding X matrix. The sums of squares and cross-products matrices are

$$SSB = R_b'R_b$$

$$SSS = R_s'R_s$$

and

$$SSA = R_a'R_a$$

The degrees of freedom associated with each of the sums of squares and cross-products matrices are $b-1$, $b(s-1)$ and $bs(a-1)$, respectively. Mean square matrices are calculated by dividing the sums of squares and cross-products matrices by their respective degrees of freedom:

$$MSB = SSB/(b-1)$$

$$MSS = SSS/(bs-b)$$

$$MSA = SSA/(bsa-bs)$$

The expected values of the mean square matrices are

$$E(MSB) = \Sigma_A + \Sigma_S + a*s*tr(PP')*\Sigma_B/b$$

$$E(MSS) = \Sigma_A + a*\Sigma_S$$

$$E(MSA) = \Sigma_A$$

where $P = P_f$ for the CFMUT and $P_m P_f$ for the MFT and $tr(PP')$ denotes the trace of PP' . The matrices P_f and P_m are formed according to Equation (B.2.2) of Appendix B. Equating the mean square matrices with their expected values forms a linear system of three equations in three unknowns where the

unknowns are 8x8 matrices. Back solving this system of equations provides unbiased estimates of the three covariance matrices due to batches, samples and analyses.

Since the estimation and process control schemes given in Appendix B require $E(MSS)/(as)$, it is not necessary to estimate SS separately because recombining the estimates of Σ_A and Σ_S will yield $M\Sigma_S/(as)$.

The data from both the CFMUT and the MFT can be combined to get estimates based on more information. If the number of samples per batch and the number of analyses per sample are the same for both CFMUT and MFT, then the corresponding estimate of Σ_B , Σ_S and Σ_A from both tanks can be averaged. If the number of samples per batch or the number of analyses per sample or both are different for the two tanks, then weighted averages would be more appropriate:

$$\Sigma_{Bc} = (afsf\Sigma_{Bf} + amsm\Sigma_{Bm})/(afsf+amsm)$$

$$\Sigma_{Sc} = (af\Sigma_{Sf} + am\Sigma_{Sm})/(af+am)$$

$$\Sigma_{Ac} = (\Sigma_{Af} + \Sigma_{Am})/2.$$

Batch means for each tank are estimated per Equation (B.2.10) of Appendix B.

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