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**Strategy for Product Composition
Control in the Hanford Waste
Vitrification Plant**

M.F. Bryan

G.F. Piepel

March 1996

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

Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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SUMMARY

The Hanford Waste Vitrification Plant (HWVP) will immobilize transuranic and high-level radioactive waste in borosilicate glass. The major objective of the Process/Product Model Development (PPMD) cost account of the Pacific Northwest Laboratory HWVP Technology Development (PHTD) Project is the development of a system for guiding control of feed slurry composition (which affects glass properties) and for checking and documenting product quality. This document lays out the broad structure of HWVP's product composition control system, discusses five major algorithms and technical issues relevant to this system, and sketches the path of development and testing.

GLOSSARY

Acceptable--A batch, mixture, or composition for which all applicable requirements will be met (with some degree of statistical confidence, as discussed in the body of the document).

Batch--A discrete quantity of material (waste, frit, recycle, or a combination of the three) to be processed by the Hanford Waste Vittrification Plant (HWVP).

Composition--A list of the proportions of each chemical species in a batch of material to be processed by the HWVP. Compositions are usually expressed as mass fractions of nine major oxides (SiO_2 , B_2O_3 , Na_2O , Li_2O , CaO , MgO , Fe_2O_3 , Al_2O_3 , ZrO_2) and a catchall category, Others; in some cases, individual species normally included in Others may be segregated. Cf. *mixture*.

Compositional data--A type of multivariate data in which the numerical values in each datum are the proportions (or percentages) of the individual components of the material or characteristic being represented by the datum. From their nature as proportions (percentages), these numerical values must lie between 0 and 1 (0 and 100%), inclusive, and they must sum to 1 (100%).

Contents--The mass and composition of material in a given tank.

Critical component constraints--Constraints imposed by HWVP on the mass fractions of several minor chemical species that may (e.g., for reasons of solubility) impair melter function or product acceptability.

CVS region constraints--Constraints imposed by HWVP on mass fractions of the nine major oxides and Others in the feed material; these constraints are related to the extent of the Composition Variability Study (CVS) database and are intended to discourage extrapolation of CVS property models to compositions outside the region studied by CVS.

Feed--Though technically referring to material after processing in the Slurry Mix Evaporator, *feed* or *feed material* will here be used as a generic term to refer to any material being processed by HWVP upstream of the melter itself; cf. *melt*.

Melt--Material being processed by HWVP in the melter or before it has cooled and solidified into glass. Before reaching the melter, this material will be referred to as *feed* (q.v.).

Mixture--The combination of waste, frit, and recycle constituting a batch to be processed by the HWVP. Both *mixtures* and *compositions* (q.v.) are expressed in terms of proportions of individual components, but these characterizations differ in the components used to represent the batch: a mixture is expressed in terms of the three input streams (waste, frit, and recycle), while a composition is expressed in terms of the individual chemical species, usually oxides.

Stand-in constraints--Constraints imposed on mass fractions (and functions thereof) of the ten major glass components (nine oxides and Other) that are intended to control crystallinity of the glass.

WAPS properties and requirements--Properties of and requirements on glass produced by HWVP, as detailed in the *Waste Acceptance Product Specifications* (WAPS; DOE, 1993). These properties and requirements are related to the performance of the glass in the repository.

Waste loading--The mass fraction of waste in a batch of feed or in the glass resulting therefrom.

Waste type--A relatively homogeneous stream of waste to be processed by the HWVP. Several to many *batches* (q.v.) will be made from a single waste stream, and at least one requirement will be imposed on the entire waste type, rather than on the individual batches (see *multiple-batch property*).

ACRONYMS

CVS--Composition Variability Study

DWPF--Defense Waste Processing Facility

EA--Environmental Assessment

FAA--Frit Addition Algorithm

FTA--Feed Test Algorithm

GFA--Glass Formulation Algorithm

HWVP--Hanford Waste Vitrification Plant

MEM--Measurement Error Model

MFT--Melter Feed Tank

OWL--Optimal Waste Loading methodology

PCC--the system to be used by HWVP for product composition control

PCT--Product Consistency Test

PFSFT--Process Frit Slurry Feed Tank

PHTD--Pacific Northwest Laboratory (PNL) HWVP Technology Development

PPMD--Process/Product Model Development

RWCT--Recycle Waste Collection Tank

SME--Slurry Mix Evaporator

SRA--SME Remediation Algorithm

SRAT--Slurry Receipt and Adjustment Tank

STA--SME Targeting Algorithm

WAPS--Waste Acceptance Product Specifications

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1.0 INTRODUCTION

The Hanford Waste Vitrification Plant (HWVP) will immobilize transuranic and high-level radioactive waste in borosilicate glass. Similar operations will be performed in the Defense Waste Processing Facility (DWPF) at the Savannah River Site. DWPF has developed the Product Composition Control System (PCCS) for guiding control of feed slurry composition (which affects glass properties) and for checking and documenting product quality (Postles and Brown, 1991). The *HWVP Project Waste Form Qualification Program Plan* (Randklev, 1993) calls for the development of a product composition control-type code to perform these functions for the HWVP. The major objective of the Process/Product Model Development (PPMD) cost account of the Pacific Northwest Laboratory HWVP Technology Development (PHTD) Project is the development of such a system. This document lays out the broad structure of HWVP's product composition control system, discusses technical issues and considerations relevant to this system, and sketches the path of development and testing.

No name for the HWVP product composition control system has yet been generally agreed upon. As mentioned above, the *HWVP Project Waste Form Qualification Program Plan* (Randklev, 1993) refers to this system as a product composition control-type code or PCC-type code. For brevity, PCC (from product composition control) will be used here to refer to the system under development for HWVP.

Figure 1 is a simplified representation of the structure of the HWVP as it relates to a control strategy. The heart of the HWVP comprises five tanks and a melter. The five tanks are:

- the Slurry Receipt and Adjustment Tank (SRAT), in which the main waste stream will be mixed with a reductant to control foaming in the melter;
- the Process Frit Slurry Feed Tank (PFSFT), which, as the name implies, will store fresh frit;
- the Recycle Waste Collection Tank (RWCT), in which several recycle streams (the largest of which is expected to be frit used in canister decontamination) will be collected;

- the Slurry Mix Evaporator (SME), in which waste, frit, and recycle will be mixed to form a slurry; and
- the Melter Feed Tank (MFT), which will receive slurry from the SME and will feed it to the melter.

Waste, frit, and recycle from the SRAT, PFSFT, and RWCT (respectively) will be combined in the SME, whence the resulting slurry will pass to the MFT and eventually to the melter. The SME is the last stage at which feed composition can be modified. From the melter, the molten glass (or melt) will be poured into canisters for cooling and eventual disposal in a geologic repository.

Some definitions and terminology are now in order. *Composition* will be used to refer to the chemical species (or proportions thereof) in a given material (e.g., waste, frit, recycle, and combinations of these). Compositions are usually expressed as mass fractions of nine individual oxides (SiO_2 , B_2O_3 , Na_2O , Li_2O , CaO , MgO , Fe_2O_3 , Al_2O_3 , ZrO_2) and a catchall category, Others. This convention was adopted for glass characterization studies which developed glass property models based on the oxide compositions. In some cases, individual species normally included in Others may be separately identified. The *contents* of a given tank will be used to refer to both composition and mass of material in the tank. *Mixture* denotes a combination of waste, frit, and recycle. *Batch* denotes a discrete quantity of material to be processed; HWVP will process material in batches (as opposed to a continuous stream of feed material). The main focus of the HWVP PCC will be SME batches (material residing in the SME), since this is the last stage at which feed composition can be modified. The size of each batch will be related to the capacities of the tanks used to mix the batch. Batches should fall rather naturally into groups, with the batches in each group deriving from a relatively homogeneous waste stream. This homogeneous waste stream and the batches made from it will be referred to as a *waste type*, and the processing of batches in a single waste type will be referred to as a *production campaign*.

The glass produced by HWVP must meet certain requirements for acceptance into the geologic repository. These requirements are given in the *Waste Acceptance Product Specifications* (WAPS; DOE, 1993). In addition to the WAPS requirements for the final glass, HWVP will impose requirements on properties of the melt in order to ensure

- Given information about the composition and variability of a single waste type, choose the frit composition and the optimal mixture for the entire production campaign. This mixture will be referred to as the *reference mixture* for the production campaign.
- Given the reference mixture and frit composition for the production campaign, the current composition of waste and recycle in the SRAT and RWCT, respectively, and information on various uncertainties, choose the optimal mixture for the current batch. This *target mixture* then dictates the masses of waste, recycle, and frit to transfer to the SME. The target mixture may differ from the reference mixture, due to heterogeneity in input streams and other sources of uncertainty.
- After transferring material to the SME, characterize the contents of the SME. This step is not as simple as it seems, because two sets of information are available: direct measurements of the SME, and estimates of SME composition derived from information on compositions and masses of material transferred from the source tanks (SRAT, PFSFT, and RWCT). These two sets of information must be reconciled.
- Test the acceptability of the SME composition.
- If the SME composition is deemed unacceptable, choose the most efficient remediation strategy.

The HWVP PCC will employ one major mathematical/statistical algorithm for each of these steps. These main algorithms are discussed in Section 3. Supporting algorithms and technical issues are discussed in Section 4. Finally, the status and development path proposed for the HWVP PCC are discussed in Section 5.

1.2 WHY STATISTICAL PROCESS CONTROL?

The HWVP PCC will be a statistical process control system, in that uncertainties will be accounted for in making decisions. The term *statistical process control* is often used to refer to the statistical techniques used in monitoring a process (e.g., control charts), but here this term is applied in a broader sense to a system that will make concrete decisions and recommendations about the actual operation of the plant (as sketched in Section 1.1). This section explains the need for and role of statistics in designing and implementing the PCC.

important in identifying efficient decision-making procedures with satisfactory error rates, in choosing among competing decision-making procedures, in exploring tradeoffs between the two error rates, in choosing and allocating efforts to obtain data (how many samples? how many measurements per sample?), and in attaching statistical "confidence" (which is intimately related to one of the two error rates) to decisions. In addition, statistical methods are important in estimating various sources of uncertainty, and in properly combining these sources and propagating them through property models in order to establish the reliability of the prediction. (Of course, development and validation of property models require extensive use of statistical methods, but this activity is currently separate from development of the HWVP PCC.) *Thus, due to the several inevitable uncertainties and variabilities in the HWVP system, statistics has a major role to play in the PCC and in the design thereof.*

2.0 MELT AND GLASS PROPERTIES, MODELS, AND CONSTRAINTS

As mentioned in Section 1, models are being developed to relate feed composition to melt and glass properties. These models will be used in: (1) targeting acceptable mixtures of waste, frit, and recycle, (2) testing the acceptability of SME batches, and (3) identifying remediation strategies for unacceptable batches. The development of property models is one of the objectives of the Composition Variability Study (CVS), in which glasses of known composition are fabricated and properties of these glasses (and the melts used to produce the glasses) are measured. The CVS is described in detail by Hrma and Piepel (1992), from which much of the following discussion is taken.

Requirements or constraints will be imposed on three broad categories of properties:

- properties that affect performance of the final glass in the repository and for which requirements are imposed by the WAPS (these will be referred to as *WAPS properties and requirements*);
- properties that affect processability of the material and for which requirements are imposed by the HWVP project (these will be referred to as *processability properties, constraints, and requirements*); and
- the composition of the feed itself, upon which are imposed the *CVS region constraints*;

the glass, which is related to liquidus temperature. When satisfactory models become available for liquidus temperature and crystallinity behavior, the stand-in constraints may still be active as CVS region constraints, due to the role the stand-in constraints have played in defining the CVS experimental program. Redox rate may be directly measured, and work is underway on phase separation and melt rate, but these properties will not be further addressed here. *Critical component constraints* are upper bounds on mass fractions of several minor species that may impair melter function for some reason (e.g., solubility).

The current *reference constraint set*, to be used in identifying acceptable compositions, appears in Table 1. Not all of the properties, requirements, and constraints discussed above are included in the reference constraint set. This set is subject to modification as requirements change, the CVS database grows (which may relax some of the CVS region constraints), and new CVS property models become available. Table 2 lists problematic constraints (those for which satisfactory models are not available, or for which the modelling approach may not be appropriate and no other approach has been developed).

Table 1. Current Reference Constraint Set

Category	Constraint(s)	Explanation
WAPS	WAPS 1.3 Product Consistency Test	Li, Na, B concentrations less than those of the EA glass
Processability	Viscosity at 1150°C	2 - 10 Pa·s
Processability	Electrical conductivity at 1150°C	18-111 S/m
Processability	Stand-in constraints (crystallinity)	Five constraints expressed as functions of major components
Processability	Critical component constraints (solubility)	Upper bounds on mass fractions of Cr ₂ O ₃ , F, P ₂ O ₅ , SO ₃ , and oxides of Rh, Pd, and Ru
CVS Region	SiO ₂ , B ₂ O ₃ , Na ₂ O, Li ₂ O, CaO, MgO, Fe ₂ O ₃ , Al ₂ O ₃ , ZrO ₂ , Others	Lower and upper limits on each of the ten CVS components

3.1 GLASS FORMULATION ALGORITHM (GFA)

The Glass Formulation Algorithm (GFA) will select the reference mixture and frit composition for an entire production campaign. One possible choice for the reference mixture is the blend of waste, recycle, and frit that would be expected to maximize waste loading of the resulting glass *if each input stream were perfectly homogeneous*. Alternatively, given an estimate of the heterogeneity of the waste type, the reference mixture and frit composition might be adjusted in an attempt to buffer against the most serious probable deviations from acceptability.

The reference mixture will be used as a starting point in selecting the target mixtures for individual batches in a production campaign. Full maximization (subject, of course, to applicable requirements and constraints) of waste loading for each batch may not be possible, because the WAPS 1.3 product consistency requirement must be controlled over an entire waste type (the control of such *multiple-batch properties* is discussed in more detail in Section 4.5). The reference mixture will serve to "leash" the individual batch compositions to a central point for the entire waste type.

Mathematically, the task of the GFA is an optimization problem, and the GFA will draw upon the work done in developing and applying the Optimal Waste Loading (OWL) methodology (Hoza, 1993). The optimization done in OWL is more extensive than that required by the PCC (for example, OWL is being used to investigate blending of waste types, while the PCC will have no control over the waste type presented to it), but the mathematical techniques required by PCC to select frit composition and the reference mixture for a single waste type should be very similar to a subset of the OWL methodology.

The GFA must take into account mass, composition, and estimated uncertainty for the waste type, and feed/melt/glass property requirements, models, and uncertainties. In addition, the GFA may account for recycle composition. OWL uses a simplified HWVP flowsheet simulation to obtain recycle composition. For the GFA, the simplest approach is to assume that recycle will be a fixed mixture of waste, frit, and other chemical species arising in HWVP processing.

SME heel; feed/melt/glass property requirements, models, and uncertainties; the reference mixture for this production campaign; properties and/or compositions of preceding batches in this campaign; and any other constraints on the candidate mixtures (e.g., HWVP may be required to use recycle at the rate it is produced or to keep recycle volume below some limit, effectively forcing each SME batch to accommodate some minimum amount of recycle).

Other capabilities that should be considered in designing the STA include the ability to "learn from its mistakes." For example, as experience with a given waste type accumulates, the algorithm may be able to identify the most common deviations of actual mixtures from recommended mixtures and to assign priorities to these deviations (i.e., to decide which are most difficult to remediate and therefore should be avoided). This implies a link between the STA and other main PCC algorithms, as well as links to an accumulating database on the current production campaign (Section 4.6) and to process monitoring algorithms (Section 4.7).

A preliminary version of the STA, known as the Frit Addition Algorithm (FAA), has been developed and implemented.

3.4 FEED TEST ALGORITHM (FTA)

The Feed Test Algorithm (FTA) will decide whether a particular SME batch is acceptable by comparing estimates of SME composition and glass/melt properties to the requirements discussed in Section 2. These comparisons must take into account various types and sources of uncertainty. Inputs to the FTA include estimates of SME composition and uncertainty, feed/melt/glass property requirements, models, and uncertainties, and information on the reference mixture and previous batches in the current production campaign. A preliminary FTA has been developed; see Bryan and Piepel (1993) for more information. Future versions of the FTA may incorporate remediability and other constraints on candidate mixtures.

3.5 SME REMEDIATION ALGORITHM (SRA)

The SME Remediation Algorithm (SRA) will come into play when the FTA identifies an unacceptable SME batch. The SRA must then identify the troublesome properties and requirements and must choose a remediation strategy. This is again an optimization problem,

Table 4. Technical Issues to be Addressed in Development of the HWVP PCC

Group of Issues	Description of Group
Compositional data	Effects on proposed statistical methods and algorithms; statistical models and distributions; optimal normalization to 100 wt%
Estimation of tank contents	Estimating tank contents and uncertainty from indirect measurements; combining and reconciling several sources of information on tank contents; estimating increase in precision
Estimation of covariance matrices	Methods for estimating covariance matrices and components of covariance; obtaining data and estimating matrices; efficiency and implications for required sampling effort
Recognizing acceptable compositions	Generally applicable method for ascertaining whether a given composition is acceptable, given relevant sources of uncertainty
Controlling multiple-batch properties	Methods for controlling properties (e.g., WAPS 1.3) for which compliance must be demonstrated over a group of batches
Database of operating experience	Establishing, maintaining, accessing, and updating a database of operating experience
Process monitoring	Methods and algorithms for process monitoring (e.g., control charts)
Control of sampling effort	Methods and algorithms for level and allocation of sampling effort
Bias detection and correction	Methods and algorithms for detection and correction of bias in analytical measurements

defining feature of compositional data and the source of technical difficulties associated with compositional data.

Briefly, the unit-sum restriction inherent in compositional data implies that compositional data cannot follow a multivariate normal (Gaussian) distribution. The best known statistical techniques are demonstrably optimal only for normally-distributed data. While it is likely that these and other statistical techniques will perform adequately for

sources of information on tank contents (e.g., information for source and recipient tanks before and after transfers); and (3) estimating the expected increase in precision from this combination of information. Several aspects of these issues have been addressed in the existing MEM, but some of the solutions may require revision as more is learned about the nature of the compositional data involved in the PCC. In addition, estimating the increase in precision from combining information will require the uncertainty estimates (covariance matrices) discussed next.

4.3 ESTIMATION OF COVARIANCE MATRICES

Covariance matrices are used to express uncertainty and interdependencies in multivariate data. *Estimation of covariance matrices* from adequate raw data is a straightforward task, but, under some circumstances, "adequate" data may be difficult to obtain. This may have consequences for the amount and quality of data that will be available for the PCC. In addition, given the hierarchical nature (waste types, batches within waste type, samples within batch, analyses within sample) of the sources of uncertainty, proper uncertainty estimation and error propagation will require estimation of *covariance components*, which essentially divide overall uncertainty among the levels in the hierarchy. The segmented nature (several discrete tanks) of the HWVP system may necessitate separate estimation of covariance matrices (and covariance components) for the various segments of the process. Possible sources of data must be identified, the data obtained, and the actual estimation performed. Where adequate data are not available, it may be possible to develop estimates from assumptions about the sampling and analytical processes. All of these issues may be affected by the compositional nature of much of the PCC data. See Bryan et al. (1993b) for more discussion.

4.4 RECOGNIZING ACCEPTABLE COMPOSITIONS

Recognizing acceptable compositions is at the heart of the PCC. In some sense, all of the major algorithms except the MEM must be able to ascertain whether a candidate composition is acceptable, i.e., whether all relevant properties can be shown to meet applicable requirements, given estimates of relevant uncertainties (although which properties,

compliance over the production campaign. The severity of this restriction on optimal waste loading will be strongly affected by the estimated covariance components, specifically the batch-to-batch variability in composition, which is related to heterogeneity in the waste stream.

The most important example of a multiple-batch property is the WAPS 1.3 product consistency requirement: "One acceptable method of demonstrating that the acceptance criterion is met ... would be to ensure that the mean PCT results *for each waste type* are at least two standard deviations below the mean PCT results of the EA glass" (DOE, 1993; italics added). Therefore, the issue of controlling multiple-batch properties is intimately involved with demonstrating compliance with the WAPS 1.3 requirement. See Bryan et al. (1993a) for a more detailed discussion of controlling multiple-batch properties, with specific reference to the WAPS 1.3 requirement.

4.6 DATABASE OF OPERATING EXPERIENCE

A *database of operating experience* must be established in order to provide either prior estimates of, or data from which to estimate, covariance matrices and other quantities required by the PCC. Questions of when and how to update and access this database must be addressed. For example, should the PCC have access to all operating experience, or only to that somehow deemed relevant to the current waste type? What is the relevant set? More specifically, should the current set of measurements be added to the database before or after calculations are performed with this set of measurements? Finally, the format of the database must evolve with the algorithms and estimation methods.

4.7 OTHER ISSUES

The last three groups of issues, *process monitoring*, *control of sampling effort*, and *bias detection and correction*, will be very important in plant operation, but work on these issues can be delayed until more is known about the issues above and about the final design of the HWVP. Each will result in algorithms to be added to the PCC, and each algorithm may require access to the database of operating experience. Process monitoring will include routine monitoring of plant operations, utilizing the standard tools of statistical process control

Table 5. Status of Development of the Major PCC Algorithms

Algorithm	Preliminary Version	Implemented	Comments
GFA	No	No	Requires mathematical optimization routine
MEM	Yes	Yes	
STA	Yes	Yes	Requires mathematical optimization routine; existing preliminary version known as the Frit Addition Algorithm
FTA	Yes	No	Implementation in FY 94
SRA	No	No	Requires mathematical optimization routine

- Implement FTA in Plant Simulation Code. This will allow commencement of testing of existing algorithms and other activities important to development and design of the HWVP PCC. See the discussion of the Plant Simulation Code, below.
- Address issues related to compositional data, since this type of data permeates the HWVP PCC, and its properties are not well understood. Testing of existing algorithms using the Plant Simulation Code may identify troublesome aspects of compositional data.
- Obtain or construct *and document* reasonable estimates (e.g., covariance matrices) for various sources of uncertainty. This will aid in testing with the Plant Simulation Code and is prerequisite to resolving several of the outstanding technical issues.
- Update the existing FAA to the STA, and implement this STA in the Plant Simulation Code. The routines that perform the mathematical optimization in the STA should be modular, as they may be required by the GFA and the SRA.

Near term testing of algorithms developed by PPMD will be accomplished by incorporating them into the Plant Simulation Code, a large, complex FORTRAN program designed to simulate HWVP operations. The Plant Simulation Code is discussed in more detail by Kuhn (1992). Among the roles of this software in development and design of the HWVP is the verification of PCC algorithms. Verification will be initiated by testing the

- Run the FAA (or the STA when available) to choose a target mixture.
- "Make" the chosen mixture (with or without mixing error) and "measure" it (i.e., contaminate the "known" parameters of the mixture with random "noise" to simulate sampling and analytical uncertainties).
- Use MEM to produce an estimate of the "true" SME composition.
- Use FTA to decide whether the estimated composition is acceptable.

For each simulated run, the "true" SME composition and the judgement of the FTA will be tallied. After performing as many runs as is practical, the results will be examined. The simplest measure would be a 2x2 table, tabulating the number of FTA-predicted "good" and "bad" batches against the known "true" status of the simulated mixture. By controlling the various uncertainties introduced in the simulation, performance of the various algorithms can be examined. For example, with no simulated randomness in the "processing" of the batch (i.e., in the differential equations used by the Plant Simulation Code), with fixed input waste, frit, and recycle compositions, with no measurement error, and with mixing without error, the resulting mixture can be "bad" only if the FAA (or STA) fails to choose a good target. Thus, the proportion of "true bad" batches is an indication of the failure rate of the STA. In addition, the proportion of "true good, predicted bad" results is a measure of the false alarm rate of the FTA, while the proportion of "true bad, predicted good" batches is a measure of the sensitivity of the FTA to bad batches.

The above discussion of the use of the Plant Simulation Code to test the PCC algorithms centered on the existing algorithms (MEM, FAA, and FTA). The technique can be extended to testing of the STA, GFA, and SRA when these algorithms become available. (As noted in Section 3, the SRA might logically be incorporated into the FTA. However, the FTA is prerequisite to the SRA, but not vice versa; this and the increased simplicity of testing the two algorithms separately have resulted in the separation of the two algorithms.) In addition, *when well-founded estimates of various sources of uncertainty are available*, these techniques can be used to examine the efficacy and efficiency of various strategies for sampling and analyzing material in the HWVP process.

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**Strategy for Product Composition
Control in the Hanford Waste
Vitrification Plant**

M.F. Bryan

G.F. Piepel

March 1996

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

Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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SUMMARY

The Hanford Waste Vitrification Plant (HWVP) will immobilize transuranic and high-level radioactive waste in borosilicate glass. The major objective of the Process/Product Model Development (PPMD) cost account of the Pacific Northwest Laboratory HWVP Technology Development (PHTD) Project is the development of a system for guiding control of feed slurry composition (which affects glass properties) and for checking and documenting product quality. This document lays out the broad structure of HWVP's product composition control system, discusses five major algorithms and technical issues relevant to this system, and sketches the path of development and testing.

GLOSSARY

Acceptable--A batch, mixture, or composition for which all applicable requirements will be met (with some degree of statistical confidence, as discussed in the body of the document).

Batch--A discrete quantity of material (waste, frit, recycle, or a combination of the three) to be processed by the Hanford Waste Vitrification Plant (HWVP).

Composition--A list of the proportions of each chemical species in a batch of material to be processed by the HWVP. Compositions are usually expressed as mass fractions of nine major oxides (SiO_2 , B_2O_3 , Na_2O , Li_2O , CaO , MgO , Fe_2O_3 , Al_2O_3 , ZrO_2) and a catchall category, Others; in some cases, individual species normally included in Others may be segregated. Cf. *mixture*.

Compositional data--A type of multivariate data in which the numerical values in each datum are the proportions (or percentages) of the individual components of the material or characteristic being represented by the datum. From their nature as proportions (percentages), these numerical values must lie between 0 and 1 (0 and 100%), inclusive, and they must sum to 1 (100%).

Contents--The mass and composition of material in a given tank.

Critical component constraints--Constraints imposed by HWVP on the mass fractions of several minor chemical species that may (e.g., for reasons of solubility) impair melter function or product acceptability.

CVS region constraints--Constraints imposed by HWVP on mass fractions of the nine major oxides and Others in the feed material; these constraints are related to the extent of the Composition Variability Study (CVS) database and are intended to discourage extrapolation of CVS property models to compositions outside the region studied by CVS.

Feed--Though technically referring to material after processing in the Slurry Mix Evaporator, *feed* or *feed material* will here be used as a generic term to refer to any material being processed by HWVP upstream of the melter itself; cf. *melt*.

Melt--Material being processed by HWVP in the melter or before it has cooled and solidified into glass. Before reaching the melter, this material will be referred to as *feed* (q.v.).

Mixture--The combination of waste, frit, and recycle constituting a batch to be processed by the HWVP. Both *mixtures* and *compositions* (q.v.) are expressed in terms of proportions of individual components, but these characterizations differ in the components used to represent the batch: a mixture is expressed in terms of the three input streams (waste, frit, and recycle), while a composition is expressed in terms of the individual chemical species, usually oxides.

Monte Carlo technique--Method for obtaining an approximate solution to a problem in which the exact mathematical manipulations are difficult or intractable. A *Monte Carlo solution* is obtained via numerous runs of a stochastic simulation, i.e., a simulation of the process under investigation, in which each inexact quantity is replaced by a randomly-generated value, centered on the best estimate of the quantity and varying in direct proportion to the uncertainty about the true value. See Kennedy and Gentle (1980) or Ripley (1987) for information on Monte Carlo methods and stochastic simulation.

Multiple-batch property--A property for which a requirement is imposed over a set of batches to be processed by the HWVP; e.g., a property for which the requirement is imposed on an entire *waste type* (q.v.), rather than on the individual batches constituting the waste type. In contrast, most requirements and constraints on the material processed by HWVP are imposed only on the current batch, with no reference to the characteristics of preceding or succeeding batches.

Optimal mixture--The mixture of waste, frit, and recycle that results in optimal waste loading (q.v.).

Optimal waste loading--For the purposes of this document, *optimal waste loading* is defined as the maximum waste loading consistent with the ability to demonstrate compliance with all requirements and constraints imposed on HWVP feed, melt, and glass. Due to the various uncertainties involved in demonstrating compliance, optimal waste loading may be somewhat less than the absolute maximum consistent with compliance.

Processability properties and requirements--Properties of and requirements on HWVP feed material that are related to the ability to process the material effectively, efficiently, and without damage to equipment.

Production campaign--The processing of all batches in a single *waste type* (q.v.).

Reference constraint set--The current set of requirements and constraints to be imposed on HWVP feed, melt, and glass. This set will be used to target and identify acceptable batches and to identify remediation strategies for unacceptable batches.

Reference mixture--The mixture of waste, frit, and recycle that will serve as the starting point for deriving the *target mixture* (q.v.) for an individual batch in a single waste type. The *reference mixture* applies to an entire waste type or production campaign, will be determined before commencement of the production campaign, and will remain fixed for the entire production campaign.

Target mixture--The mixture of waste, frit, and recycle that will maximize waste loading for an individual batch of material, subject to various requirements and constraints and to the uncertainties involved in demonstrating compliance with these requirements and constraints. Due to heterogeneity in input streams and other sources of uncertainty, the *target mixture* may differ from the *reference mixture* (q.v.) for the production campaign.

Stand-in constraints--Constraints imposed on mass fractions (and functions thereof) of the ten major glass components (nine oxides and Other) that are intended to control crystallinity of the glass.

WAPS properties and requirements--Properties of and requirements on glass produced by HWVP, as detailed in the *Waste Acceptance Product Specifications* (WAPS; DOE, 1993). These properties and requirements are related to the performance of the glass in the repository.

Waste loading--The mass fraction of waste in a batch of feed or in the glass resulting therefrom.

Waste type--A relatively homogeneous stream of waste to be processed by the HWVP. Several to many *batches* (q.v.) will be made from a single waste stream, and at least one requirement will be imposed on the entire waste type, rather than on the individual batches (see *multiple-batch property*).

ACRONYMS

CVS--Composition Variability Study

DWPF--Defense Waste Processing Facility

EA--Environmental Assessment

FAA--Frit Addition Algorithm

FTA--Feed Test Algorithm

GFA--Glass Formulation Algorithm

HWVP--Hanford Waste Vitrification Plant

MEM--Measurement Error Model

MFT--Melter Feed Tank

OWL--Optimal Waste Loading methodology

PCC--the system to be used by HWVP for product composition control

PCT--Product Consistency Test

PFSFT--Process Frit Slurry Feed Tank

PHTD--Pacific Northwest Laboratory (PNL) HWVP Technology Development

PPMD--Process/Product Model Development

RWCT--Recycle Waste Collection Tank

SME--Slurry Mix Evaporator

SRA--SME Remediation Algorithm

SRAT--Slurry Receipt and Adjustment Tank

STA--SME Targeting Algorithm

WAPS--Waste Acceptance Product Specifications

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1.0 INTRODUCTION

The Hanford Waste Vitrification Plant (HWVP) will immobilize transuranic and high-level radioactive waste in borosilicate glass. Similar operations will be performed in the Defense Waste Processing Facility (DWPF) at the Savannah River Site. DWPF has developed the Product Composition Control System (PCCS) for guiding control of feed slurry composition (which affects glass properties) and for checking and documenting product quality (Postles and Brown, 1991). The *HWVP Project Waste Form Qualification Program Plan* (Randklev, 1993) calls for the development of a product composition control-type code to perform these functions for the HWVP. The major objective of the Process/Product Model Development (PPMD) cost account of the Pacific Northwest Laboratory HWVP Technology Development (PHTD) Project is the development of such a system. This document lays out the broad structure of HWVP's product composition control system, discusses technical issues and considerations relevant to this system, and sketches the path of development and testing.

No name for the HWVP product composition control system has yet been generally agreed upon. As mentioned above, the *HWVP Project Waste Form Qualification Program Plan* (Randklev, 1993) refers to this system as a product composition control-type code or PCC-type code. For brevity, PCC (from product composition control) will be used here to refer to the system under development for HWVP.

Figure 1 is a simplified representation of the structure of the HWVP as it relates to a control strategy. The heart of the HWVP comprises five tanks and a melter. The five tanks are:

- the Slurry Receipt and Adjustment Tank (SRAT), in which the main waste stream will be mixed with a reductant to control foaming in the melter;
- the Process Frit Slurry Feed Tank (PFSFT), which, as the name implies, will store fresh frit;
- the Recycle Waste Collection Tank (RWCT), in which several recycle streams (the largest of which is expected to be frit used in canister decontamination) will be collected;

FIGURE 1. Simplified Depiction of the Heart of the HWVP

- the Slurry Mix Evaporator (SME), in which waste, frit, and recycle will be mixed to form a slurry; and
- the Melter Feed Tank (MFT), which will receive slurry from the SME and will feed it to the melter.

Waste, frit, and recycle from the SRAT, PFSFT, and RWCT (respectively) will be combined in the SME, whence the resulting slurry will pass to the MFT and eventually to the melter. The SME is the last stage at which feed composition can be modified. From the melter, the molten glass (or melt) will be poured into canisters for cooling and eventual disposal in a geologic repository.

Some definitions and terminology are now in order. *Composition* will be used to refer to the chemical species (or proportions thereof) in a given material (e.g., waste, frit, recycle, and combinations of these). Compositions are usually expressed as mass fractions of nine individual oxides (SiO_2 , B_2O_3 , Na_2O , Li_2O , CaO , MgO , Fe_2O_3 , Al_2O_3 , ZrO_2) and a catchall category, Others. This convention was adopted for glass characterization studies which developed glass property models based on the oxide compositions. In some cases, individual species normally included in Others may be separately identified. The *contents* of a given tank will be used to refer to both composition and mass of material in the tank. *Mixture* denotes a combination of waste, frit, and recycle. *Batch* denotes a discrete quantity of material to be processed; HWVP will process material in batches (as opposed to a continuous stream of feed material). The main focus of the HWVP PCC will be SME batches (material residing in the SME), since this is the last stage at which feed composition can be modified. The size of each batch will be related to the capacities of the tanks used to mix the batch. Batches should fall rather naturally into groups, with the batches in each group deriving from a relatively homogeneous waste stream. This homogeneous waste stream and the batches made from it will be referred to as a *waste type*, and the processing of batches in a single waste type will be referred to as a *production campaign*.

The glass produced by HWVP must meet certain requirements for acceptance into the geologic repository. These requirements are given in the *Waste Acceptance Product Specifications* (WAPS; DOE, 1993). In addition to the WAPS requirements for the final glass, HWVP will impose requirements on properties of the melt in order to ensure

processability. These and other requirements are discussed in Section 2. An *acceptable* SME composition, batch, or mixture is defined as one for which **all** requirements are satisfied.

As stated above, the SME is the last stage of the process at which feed composition can be modified, but most requirements on the HWVP process and product are imposed on properties that arise *after* SME processing. In other words, the HWVP PCC must use "upstream" knowledge to control "downstream" properties. In addition, the radioactive nature of the material involved in actual HWVP operation will greatly increase difficulties and risks in handling the material, and some of the properties are difficult to measure directly. In response to these considerations, HWVP is developing models to relate more easily and safely estimable quantities (e.g., feed composition) to these properties. These models, also discussed in Section 2, can then be used to identify acceptable compositions. Identification of acceptable compositions is the backbone of the PCC.

One tenet of the HWVP PCC is to control glass and melt properties by controlling feed composition. The PCC: (1) will target acceptable mixtures, (2) will use measured quantities and property models to test whether each batch is acceptable, and (3) will recommend remediation strategies for batches deemed unacceptable.

1.1 GENERAL DESCRIPTION OF PRODUCT COMPOSITION CONTROL

In order to minimize production and disposal costs, it is obviously desirable to maximize the waste loading of HWVP glass. Although the problem is somewhat more complicated, *optimal waste loading* is here defined as *the maximum waste loading consistent with the ability to demonstrate compliance with all requirements*, and the *optimal mixture* is defined as the mixture that results in optimal waste loading.

The HWVP PCC will draw on information about composition of the waste type, contents of process tanks, and various sources of uncertainty. This information will come from sampling and analysis of material drawn from the waste stream and the tanks themselves. (The actual sampling and analysis procedures are not discussed in this document, but control of sampling effort and allocation is discussed briefly in Section 4.7.) The PCC will entail five major steps:

- Given information about the composition and variability of a single waste type, choose the frit composition and the optimal mixture for the entire production campaign. This mixture will be referred to as the *reference mixture* for the production campaign.
- Given the reference mixture and frit composition for the production campaign, the current composition of waste and recycle in the SRAT and RWCT, respectively, and information on various uncertainties, choose the optimal mixture for the current batch. This *target mixture* then dictates the masses of waste, recycle, and frit to transfer to the SME. The target mixture may differ from the reference mixture, due to heterogeneity in input streams and other sources of uncertainty.
- After transferring material to the SME, characterize the contents of the SME. This step is not as simple as it seems, because two sets of information are available: direct measurements of the SME, and estimates of SME composition derived from information on compositions and masses of material transferred from the source tanks (SRAT, PFSFT, and RWCT). These two sets of information must be reconciled.
- Test the acceptability of the SME composition.
- If the SME composition is deemed unacceptable, choose the most efficient remediation strategy.

The HWVP PCC will employ one major mathematical/statistical algorithm for each of these steps. These main algorithms are discussed in Section 3. Supporting algorithms and technical issues are discussed in Section 4. Finally, the status and development path proposed for the HWVP PCC are discussed in Section 5.

1.2 WHY STATISTICAL PROCESS CONTROL?

The HWVP PCC will be a statistical process control system, in that uncertainties will be accounted for in making decisions. The term *statistical process control* is often used to refer to the statistical techniques used in monitoring a process (e.g., control charts), but here this term is applied in a broader sense to a system that will make concrete decisions and recommendations about the actual operation of the plant (as sketched in Section 1.1). This section explains the need for and role of statistics in designing and implementing the PCC.

As stated in Section 1.0, acceptable compositions are those for which all requirements will be satisfied, and identification of acceptable compositions is the backbone of the PCC. Unfortunately, recognizing acceptable compositions is complicated by several factors. The major complication is the existence of various uncertainties and variabilities in operation and monitoring of the plant. Among these uncertainties and variabilities are heterogeneity in input streams, potential errors in transfer and mixing operations, variability among batches within a waste type, variability among samples drawn from the same batch, uncertainty in all process and analytical measurements, and uncertainty in the models developed to relate composition to glass/melt properties. (As the last two sentences imply, it is possible to make a technical distinction between uncertainty and variability, but the distinction is not important to this discussion. "Uncertainty" will be used in a general sense below.) The existence of such uncertainties implies that, instead of simply comparing measured or predicted values to requirements, we must ask whether it is reasonable to conclude that the unknown true property values lie within requirements, given the estimated values *and the magnitude of the uncertainties in the estimates*. (For this reason, the restriction on optimal waste loading, as defined in Section 1.1, is **not** "compliance with all requirements"; it is *"the ability to demonstrate"* this compliance.)

The uncertainties discussed above are, for all practical purposes, inevitable, and they can cause two kinds of errors in decision making: deciding that a batch is acceptable when in fact it is unacceptable; and deciding that a batch is unacceptable when in fact it is acceptable. An error of the first type might lead to damage to the melter, insufficient immobilization of radionuclides, and other problems, while an error of the second type will lead to unnecessary expenses in remediating the batch. Obviously, we would prefer to avoid these errors altogether; unfortunately, uncertainties render total avoidance impossible. (In fact, for a fixed level of sampling and analytical effort, decreasing the probability of either type of error usually implies increasing the probability of the other error.) Statistical methods enter the picture here.

Statistics is the science (and art) of making decisions in the face of uncertainty. Given a decision-making procedure, statistical methods can be used to estimate the probability of either of the two types of error discussed above. Such quantification of error rates is

important in identifying efficient decision-making procedures with satisfactory error rates, in choosing among competing decision-making procedures, in exploring tradeoffs between the two error rates, in choosing and allocating efforts to obtain data (how many samples? how many measurements per sample?), and in attaching statistical "confidence" (which is intimately related to one of the two error rates) to decisions. In addition, statistical methods are important in estimating various sources of uncertainty, and in properly combining these sources and propagating them through property models in order to establish the reliability of the prediction. (Of course, development and validation of property models require extensive use of statistical methods, but this activity is currently separate from development of the HWVP PCC.) *Thus, due to the several inevitable uncertainties and variabilities in the HWVP system, statistics has a major role to play in the PCC and in the design thereof.*

2.0 MELT AND GLASS PROPERTIES, MODELS, AND CONSTRAINTS

As mentioned in Section 1, models are being developed to relate feed composition to melt and glass properties. These models will be used in: (1) targeting acceptable mixtures of waste, frit, and recycle, (2) testing the acceptability of SME batches, and (3) identifying remediation strategies for unacceptable batches. The development of property models is one of the objectives of the Composition Variability Study (CVS), in which glasses of known composition are fabricated and properties of these glasses (and the melts used to produce the glasses) are measured. The CVS is described in detail by Hrma and Piepel (1992), from which much of the following discussion is taken.

Requirements or constraints will be imposed on three broad categories of properties:

- properties that affect performance of the final glass in the repository and for which requirements are imposed by the WAPS (these will be referred to as *WAPS properties and requirements*);
- properties that affect processability of the material and for which requirements are imposed by the HWVP project (these will be referred to as *processability properties, constraints, and requirements*); and
- the composition of the feed itself, upon which are imposed the *CVS region constraints*;

these constraints are essentially the limits of the composition region explored by CVS and are necessary because of the danger inherent in extrapolating models developed from the CVS database to compositions outside the range of compositions examined by the CVS.

The major WAPS requirement is imposed by WAPS 1.3 on "product consistency," as measured by the Product Consistency Test (PCT; Jantzen, 1992b). The PCT measures the quantities of lithium, sodium, and boron leached from ground glass. The WAPS requires that "the mean concentrations of lithium, sodium and boron in the leachate ... shall each be less than those of the" Environmental Assessment (EA) benchmark glass, described in Jantzen (1992a). The WAPS 1.3 requirement is the major example of a multiple-batch property; such properties are defined and discussed in Section 4.5.

The WAPS also imposes requirements on properties of the canistered waste form, and it requires *reporting* of other glass properties (i.e., no requirements are imposed on the properties themselves; only *reporting* of the properties is required). Properties of the canistered waste form upon which requirements are imposed include free liquid, gas, explosiveness, pyrophoricity, combustibility, organic materials, chemical compatibility, heat generation, maximum dose rate, and subcriticality. These properties are not expected to be limiting and are not considered further here. Among the properties for which reporting is required are chemical composition, crystalline phases, radionuclide inventory, phase stability information (glass transition temperature and a time-temperature-transformation diagram), and results of the Toxicity Characteristic Leaching Procedure. Since only reporting of these properties is required, they play no role in identification of acceptable compositions and are not considered further here.

Processability requirements include those on viscosity at 1150°C, electrical conductivity at 1150°C, liquidus temperature (possibly separate requirements for different crystalline phases), phase separation, melt rate, redox state (Fe^{++}/Fe), and critical components. CVS has constructed satisfactory models for viscosity and electrical conductivity. Liquidus temperature is problematic at this time. *Stand-in constraints* on functions of the ten major glass components (nine oxide species and Others) have been used to address crystallinity of

the glass, which is related to liquidus temperature. When satisfactory models become available for liquidus temperature and crystallinity behavior, the stand-in constraints may still be active as CVS region constraints, due to the role the stand-in constraints have played in defining the CVS experimental program. Redox rate may be directly measured, and work is underway on phase separation and melt rate, but these properties will not be further addressed here. *Critical component constraints* are upper bounds on mass fractions of several minor species that may impair melter function for some reason (e.g., solubility).

The current *reference constraint set*, to be used in identifying acceptable compositions, appears in Table 1. Not all of the properties, requirements, and constraints discussed above are included in the reference constraint set. This set is subject to modification as requirements change, the CVS database grows (which may relax some of the CVS region constraints), and new CVS property models become available. Table 2 lists problematic constraints (those for which satisfactory models are not available, or for which the modelling approach may not be appropriate and no other approach has been developed).

Table 1. Current Reference Constraint Set

Category	Constraint(s)	Explanation
WAPS	WAPS 1.3 Product Consistency Test	Li, Na, B concentrations less than those of the EA glass
Processability	Viscosity at 1150°C	2 - 10 Pa·s
Processability	Electrical conductivity at 1150°C	18-111 S/m
Processability	Stand-in constraints (crystallinity)	Five constraints expressed as functions of major components
Processability	Critical component constraints (solubility)	Upper bounds on mass fractions of Cr ₂ O ₃ , F, P ₂ O ₅ , SO ₃ , and oxides of Rh, Pd, and Ru
CVS Region	SiO ₂ , B ₂ O ₃ , Na ₂ O, Li ₂ O, CaO, MgO, Fe ₂ O ₃ , Al ₂ O ₃ , ZrO ₂ , Others	Lower and upper limits on each of the ten CVS components

Table 2. Problematic Constraints

Category	Constraint(s)	Explanation
WAPS	Properties of canistered waste form (see text)	Not expected to be limiting; not currently modeled by CVS
Processability	Liquidus temperature	CVS models under development
Processability	Phase separation, melt rate, redox state (Fe^{++}/Fe)	Work in progress

3.0 MAIN ALGORITHMS

Section 1.1 lists five major tasks of the HWVP PCC. Table 3 lists the five major mathematical/statistical algorithms required to accomplish these tasks. The algorithms are listed in order of their application in control of the HWVP. Each algorithm is discussed in more detail below.

Table 3. Major Algorithms and Tasks of the HWVP PCC

Algorithm	Acronym	Task
Glass Formulation Algorithm	GFA	Select frit composition and reference mixture for an entire production campaign.
Measurement Error Model	MEM	Estimate contents and covariances for source and recipient tanks after transfer.
SME Targeting Algorithm	STA	Select target mixture for a single SME batch. If no acceptable mixture is found, identify troublesome property, requirement, or input stream.
Feed Test Algorithm	FTA	Test SME batch for acceptability.
SME Remediation Algorithm	SRA	Identify remediation strategy for an unacceptable SME batch.

3.1 GLASS FORMULATION ALGORITHM (GFA)

The Glass Formulation Algorithm (GFA) will select the reference mixture and frit composition for an entire production campaign. One possible choice for the reference mixture is the blend of waste, recycle, and frit that would be expected to maximize waste loading of the resulting glass *if each input stream were perfectly homogeneous*. Alternatively, given an estimate of the heterogeneity of the waste type, the reference mixture and frit composition might be adjusted in an attempt to buffer against the most serious probable deviations from acceptability.

The reference mixture will be used as a starting point in selecting the target mixtures for individual batches in a production campaign. Full maximization (subject, of course, to applicable requirements and constraints) of waste loading for each batch may not be possible, because the WAPS 1.3 product consistency requirement must be controlled over an entire waste type (the control of such *multiple-batch properties* is discussed in more detail in Section 4.5). The reference mixture will serve to "leash" the individual batch compositions to a central point for the entire waste type.

Mathematically, the task of the GFA is an optimization problem, and the GFA will draw upon the work done in developing and applying the Optimal Waste Loading (OWL) methodology (Hoza, 1993). The optimization done in OWL is more extensive than that required by the PCC (for example, OWL is being used to investigate blending of waste types, while the PCC will have no control over the waste type presented to it), but the mathematical techniques required by PCC to select frit composition and the reference mixture for a single waste type should be very similar to a subset of the OWL methodology.

The GFA must take into account mass, composition, and estimated uncertainty for the waste type, and feed/melt/glass property requirements, models, and uncertainties. In addition, the GFA may account for recycle composition. OWL uses a simplified HWVP flowsheet simulation to obtain recycle composition. For the GFA, the simplest approach is to assume that recycle will be a fixed mixture of waste, frit, and other chemical species arising in HWVP processing.

3.2 MEASUREMENT ERROR MODEL (MEM)

The Measurement Error Model (MEM) estimates contents and uncertainties (expressed as covariance matrices) for both the source and the recipient tanks after a transfer operation. Inputs to the model include pre-transfer and post-transfer levels (pressure differences) in the tanks, pre-transfer composition (expressed as component concentrations) of material in each tank, post-transfer composition of the material in the recipient tank (if available; not required), masses of samples taken from each tank, and number of analyses per sample. The model incorporates several non-linear mass balance constraints, reconciles differences among the inputs (for example, the raw estimate of mass transferred out of the source tanks may not equal the raw estimate of mass transferred into the recipient tank), and produces estimates of masses, compositions (now expressed as component mass fractions, as required by the CVS property models), and covariance matrices. The algorithm involves iterative solution of a weighted least-squares problem subject to non-linear constraints. Output from the MEM serves as input to other algorithms. The general MEM algorithm has already been developed and two versions have been implemented. As discussed in Section 5, the existing MEM will need updating.

3.3 SME TARGETING ALGORITHM (STA)

The SME Targeting Algorithm (STA) will choose the target mixture for a single SME batch and will recommend the masses of waste, recycle, and frit to transfer to the SME. If no acceptable mixture is found, the STA will identify the property, requirement, input stream, or uncertainty that is interfering with acceptability. The STA must take into account distance of the recommended mixture from the reference mixture and the possible effect of this on demonstrating compliance with requirements on multiple-batch properties (see Section 4.5 for definition and discussion of multiple-batch properties).

The task of the STA is essentially a mathematical optimization problem, as is the task of the GFA. The STA will differ from the GFA in that the STA will be working with a fixed frit composition (the GFA will select a frit composition) and must deal with the inevitable heterogeneity in the waste and recycle streams. Inputs to the STA will include information on masses, compositions, and uncertainties in the SRAT, the PFSFT, the RWCT, and the

SME heel; feed/melt/glass property requirements, models, and uncertainties; the reference mixture for this production campaign; properties and/or compositions of preceding batches in this campaign; and any other constraints on the candidate mixtures (e.g., HWVP may be required to use recycle at the rate it is produced or to keep recycle volume below some limit, effectively forcing each SME batch to accommodate some minimum amount of recycle).

Other capabilities that should be considered in designing the STA include the ability to "learn from its mistakes." For example, as experience with a given waste type accumulates, the algorithm may be able to identify the most common deviations of actual mixtures from recommended mixtures and to assign priorities to these deviations (i.e., to decide which are most difficult to remediate and therefore should be avoided). This implies a link between the STA and other main PCC algorithms, as well as links to an accumulating database on the current production campaign (Section 4.6) and to process monitoring algorithms (Section 4.7).

A preliminary version of the STA, known as the Frit Addition Algorithm (FAA), has been developed and implemented.

3.4 FEED TEST ALGORITHM (FTA)

The Feed Test Algorithm (FTA) will decide whether a particular SME batch is acceptable by comparing estimates of SME composition and glass/melt properties to the requirements discussed in Section 2. These comparisons must take into account various types and sources of uncertainty. Inputs to the FTA include estimates of SME composition and uncertainty, feed/melt/glass property requirements, models, and uncertainties, and information on the reference mixture and previous batches in the current production campaign. A preliminary FTA has been developed; see Bryan and Piepel (1993) for more information. Future versions of the FTA may incorporate remediability and other constraints on candidate mixtures.

3.5 SME REMEDIATION ALGORITHM (SRA)

The SME Remediation Algorithm (SRA) will come into play when the FTA identifies an unacceptable SME batch. The SRA must then identify the troublesome properties and requirements and must choose a remediation strategy. This is again an optimization problem,

but the SRA may optimize differently than either the GFA or the STA, in that the SRA will probably look for the "easiest" (smallest/cheapest) modification of the existing SME batch that will result in acceptability. (Indeed, in some cases, the SRA may simply recommend more extensive sampling of the SME in order to reduce uncertainties.) Inputs to the SRA include all the inputs to the FTA, with which it might be incorporated. It is here kept separate from the FTA for developmental reasons (discussed in Section 5).

4.0 TECHNICAL ISSUES AND SUPPORTING ALGORITHMS

Some technical issues that have been or will be encountered in the development of the HWVP PCC affect or are related to more than one of the main PCC algorithms. Table 4 lists several groups of such technical issues and gives a short description of each group. More detailed (though still brief) discussion and references are given in the text below. In addition, candidates for supporting algorithms are identified where appropriate.

The issues included in each group are obviously strongly related, but it should be noted that there also exist strong interactions between issues in separate groups. Some of these interactions are indicated below, but others will surface during development and testing of the PCC. In addition, other issues are almost certain to arise during development of the PCC, so the list given here should not be taken to be complete or final.

4.1 COMPOSITIONAL DATA

As discussed in Section 1.0, the composition of material involved in the HWVP process will usually be quantified in terms of the mass fractions of nine individual oxides (SiO_2 , B_2O_3 , Na_2O , Li_2O , CaO , MgO , Fe_2O_3 , Al_2O_3 , ZrO_2) and a catchall category, Others. Ideally, these mass fractions should sum to one (or 100%). When this is the case, the composition is an example of *compositional data*, a type of multivariate data in which the numerical values in each datum are the proportions (or percentages) of the individual components of the material or characteristic being represented by the datum. From their nature as proportions (percentages), these numerical values must lie between 0 and 1 (0 and 100%), inclusive, and they must sum to 1 (100%). This *unit-sum restriction* is both the

Table 4. Technical Issues to be Addressed in Development of the HWVP PCC

Group of Issues	Description of Group
Compositional data	Effects on proposed statistical methods and algorithms; statistical models and distributions; optimal normalization to 100 wt%
Estimation of tank contents	Estimating tank contents and uncertainty from indirect measurements; combining and reconciling several sources of information on tank contents; estimating increase in precision
Estimation of covariance matrices	Methods for estimating covariance matrices and components of covariance; obtaining data and estimating matrices; efficiency and implications for required sampling effort
Recognizing acceptable compositions	Generally applicable method for ascertaining whether a given composition is acceptable, given relevant sources of uncertainty
Controlling multiple-batch properties	Methods for controlling properties (e.g., WAPS 1.3) for which compliance must be demonstrated over a group of batches
Database of operating experience	Establishing, maintaining, accessing, and updating a database of operating experience
Process monitoring	Methods and algorithms for process monitoring (e.g., control charts)
Control of sampling effort	Methods and algorithms for level and allocation of sampling effort
Bias detection and correction	Methods and algorithms for detection and correction of bias in analytical measurements

defining feature of compositional data and the source of technical difficulties associated with compositional data.

Briefly, the unit-sum restriction inherent in compositional data implies that compositional data cannot follow a multivariate normal (Gaussian) distribution. The best known statistical techniques are demonstrably optimal only for normally-distributed data. While it is likely that these and other statistical techniques will perform adequately for

compositional data, this should be checked during development and testing of the PCC. Theoretical and Monte Carlo investigations can be used to test the performance of various statistical techniques when applied to compositional data. (An example of a Monte Carlo study is the use of the Plant Simulation Code to study the performance of PCC algorithms; see Section 5.)

Prior to (and prerequisite for) either theoretical and Monte Carlo investigations of the effects of compositional data on statistical methods and PCC algorithms, we must identify possible statistical distributions (including covariance patterns) for the compositional data arising in HWVP. Such distributions might be derived from theoretical considerations, data, or knowledge and assumptions about the HWVP process, especially the measurement systems. Once statistical distributions have been identified, methods for generating random compositions must be developed for use in Monte Carlo testing.

At least one other issue arises in connection with compositional data. The CVS property models assume that data on feed composition will conform to the unit-sum restriction, but measured quantities may not meet the restriction. Therefore, methods for transforming non-compositional data (e.g., component concentrations) into compositional form (e.g., normalizing to 100 wt%) will be required. (The simple approach, summing components and then dividing each by the total, is not necessarily the best method.) One type of normalization is done in the existing MEM, but the MEM does much more than normalization. It is very likely that a simple, straightforward Composition Normalization Algorithm will be useful (possibly required) in development and testing of the PCC.

Aitchison (1986) discusses the underlying nature of and some statistical methods for compositional data. The applicability of Aitchison's methods to the types of compositional data arising in HWVP has not been thoroughly explored, but Aitchison's book will be a good starting point for an investigation of the role of compositional data in the HWVP PCC.

4.2 ESTIMATION OF TANK CONTENTS

Estimation of tank contents includes: (1) estimating mass, composition (oxide mass fractions), and uncertainty from indirect measurements (e.g., from pressure differences in tanks, component concentrations, etc.); (2) optimally combining and reconciling several

sources of information on tank contents (e.g., information for source and recipient tanks before and after transfers); and (3) estimating the expected increase in precision from this combination of information. Several aspects of these issues have been addressed in the existing MEM, but some of the solutions may require revision as more is learned about the nature of the compositional data involved in the PCC. In addition, estimating the increase in precision from combining information will require the uncertainty estimates (covariance matrices) discussed next.

4.3 ESTIMATION OF COVARIANCE MATRICES

Covariance matrices are used to express uncertainty and interdependencies in multivariate data. *Estimation of covariance matrices* from adequate raw data is a straightforward task, but, under some circumstances, "adequate" data may be difficult to obtain. This may have consequences for the amount and quality of data that will be available for the PCC. In addition, given the hierarchical nature (waste types, batches within waste type, samples within batch, analyses within sample) of the sources of uncertainty, proper uncertainty estimation and error propagation will require estimation of *covariance components*, which essentially divide overall uncertainty among the levels in the hierarchy. The segmented nature (several discrete tanks) of the HWVP system may necessitate separate estimation of covariance matrices (and covariance components) for the various segments of the process. Possible sources of data must be identified, the data obtained, and the actual estimation performed. Where adequate data are not available, it may be possible to develop estimates from assumptions about the sampling and analytical processes. All of these issues may be affected by the compositional nature of much of the PCC data. See Bryan et al. (1993b) for more discussion.

4.4 RECOGNIZING ACCEPTABLE COMPOSITIONS

Recognizing acceptable compositions is at the heart of the PCC. In some sense, all of the major algorithms except the MEM must be able to ascertain whether a candidate composition is acceptable, i.e., whether all relevant properties can be shown to meet applicable requirements, given estimates of relevant uncertainties (although which properties,

requirements, and uncertainties are appropriate may change from algorithm to algorithm). At a minimum, this will require methods for combining and propagating estimated uncertainties through property models. These methods may be affected by the compositional nature of the data, and certainly these methods must draw upon the uncertainty estimates (covariance matrices) discussed above. Bryan and Piepel (1993) discuss preliminary methods for recognizing acceptable compositions. The general nature and shape of the region of acceptable compositions may be of interest; for example, is the region of acceptable compositions convex? Finally, development of a single, generally applicable software "black box" for recognizing acceptable compositions (or at least for storing the most current set of property models, uncertainties, and constraints) may greatly simplify maintaining, updating, and debugging coded versions of the major algorithms.

4.5 CONTROLLING MULTIPLE-BATCH PROPERTIES

Most requirements and constraints on HWVP material apply to a single batch; i.e., most requirements are imposed on a batch-by-batch basis, so that the quality of preceding and succeeding batches does not affect the acceptability of the current batch. Such properties and requirements might be termed *single-batch properties and requirements*. In contrast, a *multiple-batch property* is one for which requirements are imposed on a set of batches (e.g., all batches derived from a single waste type). For example, if the value of Property A is required to be less than 10 for each batch, Property A is a single-batch property, whereas if the *mean value* of Property A over some set of batches is required to be less than 10, Property A is a multiple-batch property.

The problem in *controlling multiple-batch properties* arises from the necessity of accounting for variability among batches in controlling these properties. That is, owing to heterogeneity in input streams, the optimal mixture, and therefore the feed composition and related glass properties, will vary among batches in the same waste type. Optimizing waste loading separately for each batch may induce enough variability in the estimated property values to weaken the ability to statistically demonstrate compliance over the entire campaign. Therefore, some compromise must be reached between optimal waste loading in each batch and the degree of homogeneity in glass properties required to statistically demonstrate

compliance over the production campaign. The severity of this restriction on optimal waste loading will be strongly affected by the estimated covariance components, specifically the batch-to-batch variability in composition, which is related to heterogeneity in the waste stream.

The most important example of a multiple-batch property is the WAPS 1.3 product consistency requirement: "One acceptable method of demonstrating that the acceptance criterion is met ... would be to ensure that the mean PCT results *for each waste type* are at least two standard deviations below the mean PCT results of the EA glass" (DOE, 1993; italics added). Therefore, the issue of controlling multiple-batch properties is intimately involved with demonstrating compliance with the WAPS 1.3 requirement. See Bryan et al. (1993a) for a more detailed discussion of controlling multiple-batch properties, with specific reference to the WAPS 1.3 requirement.

4.6 DATABASE OF OPERATING EXPERIENCE

A *database of operating experience* must be established in order to provide either prior estimates of, or data from which to estimate, covariance matrices and other quantities required by the PCC. Questions of when and how to update and access this database must be addressed. For example, should the PCC have access to all operating experience, or only to that somehow deemed relevant to the current waste type? What is the relevant set? More specifically, should the current set of measurements be added to the database before or after calculations are performed with this set of measurements? Finally, the format of the database must evolve with the algorithms and estimation methods.

4.7 OTHER ISSUES

The last three groups of issues, *process monitoring*, *control of sampling effort*, and *bias detection and correction*, will be very important in plant operation, but work on these issues can be delayed until more is known about the issues above and about the final design of the HWVP. Each will result in algorithms to be added to the PCC, and each algorithm may require access to the database of operating experience. Process monitoring will include routine monitoring of plant operations, utilizing the standard tools of statistical process control

(e.g., control charts), producing graphical displays of plant performance, and alerting operators to unusual conditions. Algorithms for control of sampling effort will monitor results of sampling and analyses, will recommend overall sample size and allocation thereof (e.g., numbers of samples and numbers of analyses per sample), and may include routines for variable confidence and precision levels, simultaneous vs. separate statistical inference about feed/melt/glass properties, and dynamic control of sampling (i.e., the ability to recommend additional sampling of the same batch under some circumstances). Development of methods and algorithms for bias detection and correction will require extensive interaction with analytical laboratory personnel. Issues to be addressed include development and use of certified representative standards, calibration of equipment, training and monitoring of technicians, statistical (therapeutic) vs. operational (preventative) approaches, and the interface with the process monitoring system.

5.0 DEVELOPMENT STATUS AND PATH

The current development status of each major PCC algorithm is summarized in Table 5. The current status of each of the groups of technical issues discussed in Section 4 appears in Table 6. Although much has been accomplished in structuring and implementing the PCC, much remains to be done, *and all existing algorithms and resolutions for technical issues must be considered preliminary*. The major reasons for the preliminary nature of the work done so far are the lack of documented testing, the continuing evolution of the CVS models, unresolved technical issues, and the lack of good estimates of the various sources of uncertainty (required for well-founded testing of the algorithms). Since many of the technical issues are interrelated and may also affect the algorithmic approaches, the development of the PCC must be iterative in nature. That is, as remaining algorithms are developed and technical issues are resolved, some re-thinking of existing algorithms, solutions to technical issues, and documentation will become necessary. Nevertheless, it is possible to assign rough priorities to some of the remaining work. The highest priorities:

Table 5. Status of Development of the Major PCC Algorithms

Algorithm	Preliminary Version	Implemented	Comments
GFA	No	No	Requires mathematical optimization routine
MEM	Yes	Yes	
STA	Yes	Yes	Requires mathematical optimization routine; existing preliminary version known as the Frit Addition Algorithm
FTA	Yes	No	Implementation in FY 94
SRA	No	No	Requires mathematical optimization routine

- Implement FTA in Plant Simulation Code. This will allow commencement of testing of existing algorithms and other activities important to development and design of the HWVP PCC. See the discussion of the Plant Simulation Code, below.
- Address issues related to compositional data, since this type of data permeates the HWVP PCC, and its properties are not well understood. Testing of existing algorithms using the Plant Simulation Code may identify troublesome aspects of compositional data.
- Obtain or construct *and document* reasonable estimates (e.g., covariance matrices) for various sources of uncertainty. This will aid in testing with the Plant Simulation Code and is prerequisite to resolving several of the outstanding technical issues.
- Update the existing FAA to the STA, and implement this STA in the Plant Simulation Code. The routines that perform the mathematical optimization in the STA should be modular, as they may be required by the GFA and the SRA.

Near term testing of algorithms developed by PPMD will be accomplished by incorporating them into the Plant Simulation Code, a large, complex FORTRAN program designed to simulate HWVP operations. The Plant Simulation Code is discussed in more detail by Kuhn (1992). Among the roles of this software in development and design of the HWVP is the verification of PCC algorithms. Verification will be initiated by testing the

Table 6. Status of Technical Issues

Group of Issues	Development Status and Comments
Compositional data	Not well understood; potentially very important.
Estimation of tank contents	Method identified and implemented in existing MEM; estimation of increase in precision from combining various sources of information depends on well-founded estimates of uncertainty
Estimation of covariance matrices	Methods identified (Bryan et al., 1993b), but actual estimation impeded by lack of data, which also restricts examining efficiency, implications for required sampling in HWVP operation, and several other issues
Recognizing acceptable compositions	Methods exist in FAA and FTA (Bryan and Piepel, 1993); a single unified approach usable by all algorithms is desirable
Controlling multiple-batch properties	Methods described in Bryan et al. (1993a)
Database of operating experience	Unaddressed; general structure can be established by examining requirements of existing and proposed algorithms; specific structure should await more information on HWVP design
Process monitoring	Unaddressed; can await more information on HWVP design
Control of sampling effort	Unaddressed; can await more information on HWVP design
Bias detection and correction	Unaddressed; can await more information on HWVP design

algorithms with inputs for which the correct output can be obtained from other sources.

Further verification will be accomplished with Monte Carlo techniques, by performing the following steps for a number of simulated runs of the HWVP:

- Choose a "true" set of input waste oxide concentrations, and contaminate these concentrations with random "noise" to simulate various uncertainties (batch-to-batch heterogeneity, within-batch heterogeneity, sampling and analytical uncertainties).
- Generate recycle composition, based on known "true" composition and contaminated with various uncertainties.

- Run the FAA (or the STA when available) to choose a target mixture.
- "Make" the chosen mixture (with or without mixing error) and "measure" it (i.e., contaminate the "known" parameters of the mixture with random "noise" to simulate sampling and analytical uncertainties).
- Use MEM to produce an estimate of the "true" SME composition.
- Use FTA to decide whether the estimated composition is acceptable.

For each simulated run, the "true" SME composition and the judgement of the FTA will be tallied. After performing as many runs as is practical, the results will be examined. The simplest measure would be a 2x2 table, tabulating the number of FTA-predicted "good" and "bad" batches against the known "true" status of the simulated mixture. By controlling the various uncertainties introduced in the simulation, performance of the various algorithms can be examined. For example, with no simulated randomness in the "processing" of the batch (i.e., in the differential equations used by the Plant Simulation Code), with fixed input waste, frit, and recycle compositions, with no measurement error, and with mixing without error, the resulting mixture can be "bad" only if the FAA (or STA) fails to choose a good target. Thus, the proportion of "true bad" batches is an indication of the failure rate of the STA. In addition, the proportion of "true good, predicted bad" results is a measure of the false alarm rate of the FTA, while the proportion of "true bad, predicted good" batches is a measure of the sensitivity of the FTA to bad batches.

The above discussion of the use of the Plant Simulation Code to test the PCC algorithms centered on the existing algorithms (MEM, FAA, and FTA). The technique can be extended to testing of the STA, GFA, and SRA when these algorithms become available. (As noted in Section 3, the SRA might logically be incorporated into the FTA. However, the FTA is prerequisite to the SRA, but not vice versa; this and the increased simplicity of testing the two algorithms separately have resulted in the separation of the two algorithms.) In addition, *when well-founded estimates of various sources of uncertainty are available*, these techniques can be used to examine the efficacy and efficiency of various strategies for sampling and analyzing material in the HWVP process.

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