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STATISTICAL PROCESS CONTROL SUPPORT DURING DEFENSE WASTE PROCESSING FACILITY CHEMICAL RUNS

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ABSTRACT

The Product Composition Control System (PCCS) has been developed to ensure that the wasteforms produced by the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) will satisfy the regulatory and processing criteria that will be imposed. The PCCS provides rigorous, statistically-defensible management of a noisy, multivariate system subject to multiple constraints. The system has been successfully tested and has been used to control the production of the first two melter feed batches during DWPF Chemical Runs. These operations will demonstrate the viability of the DWPF process. This paper provides a brief discussion of the technical foundation for the statistical process control algorithms incorporated into PCCS, and tdescribes he results obtained and lessons learned from DWPF Cold Chemical Run operations.

The DWPF will immobilize approximately 130 million liters of high-level nuclear waste currently stored at the Site in 51 carbon steel tanks. Waste handling operations separate this waste into highly radioactive sludge and precipitate streams and less radioactive water soluble salts. (In a separate facility, soluble salts are disposed of as low-level waste in a mixture of cement, slag, and flyash.) In DWPF, the precipitate stream (Precipitate Hydrolysis Aqueous or PHA) is blended with the insoluble sludge and ground glass frit to produce melter feed slurry which is continuously fed to the DWPF melter. The melter produces a molten borosilicate glass which is poured into stainless steel canisters for cooling and, ultimately, shipment to and storage in a geologic repository.

The repository requires that the wasteform be consistently resistant to leaching by underground water that might contact it. Additionally, there are processing constraints on melt viscosity, liquidus temperature, and waste solubility that must be satisfied for the process to operate. Bad waste glass, once produced in DWPF, cannot be remedied or reworked. Thus the melter feed from which waste glass is produced must be made acceptable before it is vitrified, and the process must be controlled upstream of the melter.

The PCCS will ensure that the melt is processible and that the wasteform is acceptable. This system is an amalgam of computer hardware and software encapsulating a Statistical Process Control (SPC) Algorithm. The SPC Algorithm is used to control the multivariate DWPF process in the face of uncertainties arising from the process, its feeds, sampling, modeling, and measurement systems. This Algorithm derives optimal target blends of PHA, sludge, and frit which will combine with process heels to produce melter feed with maximum waste loading. It monitors pending melter feed batches for processibility and acceptability prior to clearing them for melting. Finally, it derives remediation blends of trim chemicals and frit to correct unacceptable melter feed batches in such a way that resulting melts will process into good product.

The PCCS has undergone extensive testing by both the developer and DWPF Technical personnel. This system has been instrumental in operating the Integrated DWPF Melter System, a pilot scale facility used in the support of startup and operation of DWPF. It has also been applied to the vitrification of actual DWPF sludge in a shielded facility at SRS. Finally, PCCS has been accepted by DWPF Technical personnel for use in both Startup and Radioactive Operation and has been successfully used to produce the first two batches of DWPF melter feed material. This material has been vitrified in crucibles (since the DWPF melter is not yet on-line) and has been shown to produce glass with acceptable product properties.

I. INTRODUCTION

The Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) will be used to blend highly radioactive insoluble sludge and precipitate (PHA) with glass-forming frit which will then be vitrified into a highly durable borosilicate wasteform (i.e., glass). The melter feed and glass must be produced in such a manner as to not be injurious to the DWPF process, especially, the melter. Furthermore, the important product and process properties that must be controlled cannot be measured in situ–they must instead be predicted from feed and glass compositions as well as melt temperature. There is no chance of rework once the glass is produced. Thus the determination of whether the glass produced is acceptable must be made on the process upstream of the melt and not on the wasteform product; therefore, DWPF control must be based upon Statistical Process Control (SPC) and not statistical quality control. An overview of the DWPF process is provided in Figure 1.[a]

The Product Composition Control System (PCCS) was developed to ensure that the product produced by DWPF will satisfy the process and product constraints imposed upon DWPF to the high degree of confidence required.[b] This assurance is obtained by controlling the composition of the slurry feed to the DWPF melter via blending and monitoring. The system defines target blends of the radioactive waste streams and the glass forming frit that maximize waste loading while simultaneously assuring to a very high degree of confidence that acceptable product is obtained. The melter feed produced is then monitored to assure that the properties projected from the measured composition are distant enough from the associated constraints to assure that the feed will produce acceptable glass. If this assurance is not forthcoming, the PCCS will provide an optimal remedy to provide acceptable melter feed.

Since acceptability depends upon projection of important properties from measured feed compositions, the decision as to whether or not melter feed will produce acceptable glass is based upon sampling, measurement, and the models used to project properties from process measurements. Sampling and measurement are both uncertain as well as the property prediction models. Furthermore, since the melter feed material must be blended, the resulting amalgam is afflicted by uncertainty in the masses transferred to produce the melter feed blend. All such uncertainties must be managed in a defensible manner in order to assure that the melter feed will indeed produce acceptable glass product. The PCCS is the vehicle which allows DWPF to produce acceptable melter feed material in the face of uncertainty.

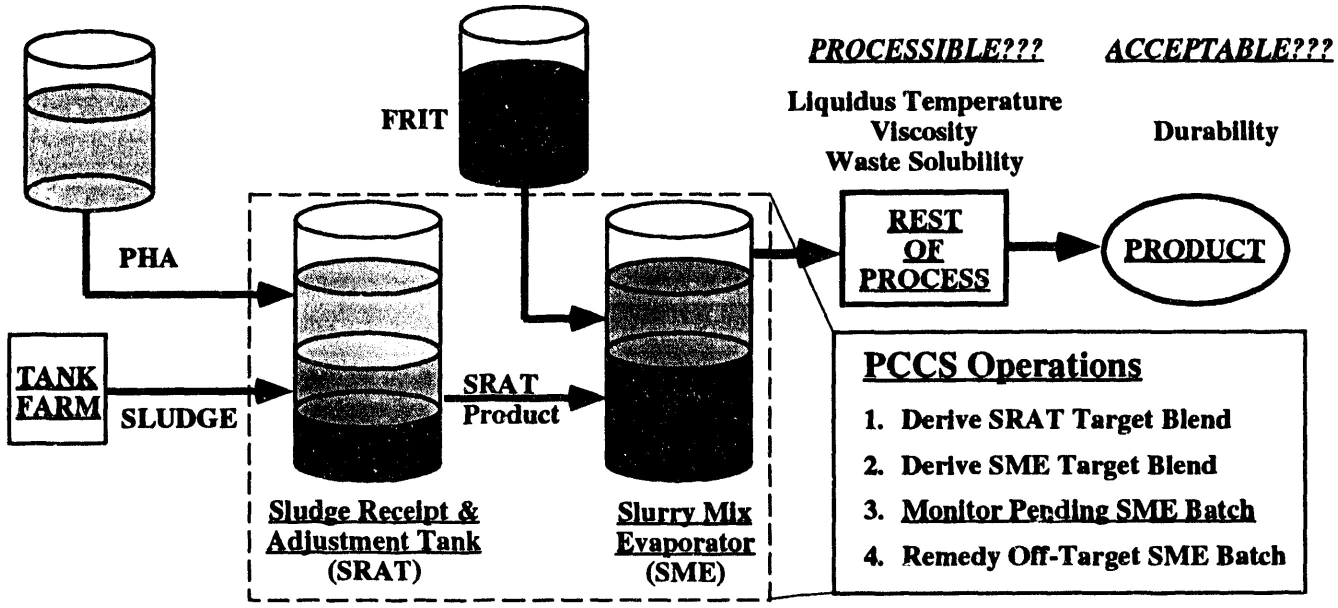

Figure 1. Schematic of the Defense Waste Processing Facility (DWPF)

II. THEORETICAL BACKGROUND

The glass produced by DWPF must be highly durable to a high degree of confidence. Thus acceptability for DWPF product is a statistical question. Glass durability is

[a] Initially the PHA and Sludge are blended and processed in an interim Sludge Receipt and Adjustment Tank (SRAT). Material from the resulting SRAT product is then transferred to the Slurry Mix Evaporator (SME) where ground glass frit is added. No further processing of the material is possible. This melter feed is then transferred to the Melter Feed Tank (MFT) which is used to continuously feed the DWPF melter.

[b] The repository mandates that the durability be acceptable to the 95% confidence level.

based upon a seven day crushed glass test (i.e., the Product Consistency Test or PCT)[1] and is thus not amenable to DWPF control. The glass durability as well as other important properties have been related to composition and melt temperature which can be measured much more readily during processing but are uncertain in nature. This implies that the composition of the feed to the DWPF melter must be controlled making DWPF process and product control multivariate in nature. The radioactive waste streams and glass-forming frit must be blended in such a way that the resulting mixture is highly likely to produce acceptable waste glass. Thus any uncertainty in material transfer must be managed as well as those in sampling, measurement, and prediction. PCCS provides a logical, rigorous treatment of these uncertainties to assure that acceptable glass is produced by DWPF.

A. Property Model Uncertainty

In order to control the DWPF properties, we must be able to predict them from process measurements. The measurement required for DWPF durability prediction is composition.[c] The glass durability (or leach rate, LR) is related to the composition via the sum of the component free energies of hydration for the major species in the waste glass:[2]

$$\ln(LR) = a + b\,\Delta \qquad (1)$$

where a and b are parameters estimated from a large database of glasses, and Δ is a rational function of the individual elemental molar oxide concentrations:

$$\Delta \equiv \sum_{\text{majors}} y_i \Delta_i = \underline{y}\,\underline{\Delta}^T \qquad (2)$$

where $\underline{y}$ and $\underline{\Delta}$ are the corresponding arrays of molar concentrations and free energies.

The observations used to define the property models do exhibit an underlying straight-line nature; however, there is scatter due to the uncertainty in the property measurement.[d] To quantify the random uncertainty in the model, Scheffé-type confidence limits are used to bound the likely location of the true relationship. The confidence curves are defined by the relationship:[3,4]

$$\text{Model Value} \pm s_r\sqrt{2\,F(2,n-2)}\sqrt{\underline{\Delta}\left(X^TX\right)^{-1}\underline{\Delta}^T} \qquad (3)$$

where s_r is the residual standard deviation, $F(2,n-2)$ is the value of the F-statistic for the number of data used to derive the model, n, $\underline{\Delta}$ is the vector $[1, \Delta]$, and (X^TX) is the product moment matrix.

Thus the property prediction models provide not only a means of relating the property to composition, they also provide a new, more stringent constraint on composition. The upper 95% confidence curve[e] is back-solved at the property (i.e., leach rate) limit providing a new constraint on composition that properly manages the modeling uncertainty.

B. Measurement Uncertainty

The compositions used to derive the property prediction models were composed of stoichiometrically compounded glasses for which the property measurement error was much greater than the error in the composition term. However during DWPF operation, the error in the composition term will no longer be negligible, in fact, it may be much greater than that in the property corresponding to the composition term. This is primarily due to the esoteric nature of the sampling, sample preparation, and analysis techniques necessary to analyze the feed slurries and determine composition.

This measurement variance is accommodated by further adjusting the composition limit for the uncertainty in the composition as measured in DWPF operation. According to equation 2, the composition term is expressible as a linear combination of the individual molar oxide concentrations. Given that there are q major elements,[f] the uncertainty associated with $\underline{y}$ is assumed q-variate Gaussian with mean $\underline{\mu}$ and covariance matrix Σ. This implies that the linear combination, $(\underline{y}\,\underline{\Delta}^T)$, is distributed as univariate Gaussian with variance $(\underline{\Delta}\,S\,\underline{\Delta}^T)$ where S is the sample estimate of Σ based upon m observations.[5] Furthermore, the quantity

[c] The melt temperature is required for other property predictions including the melt visocisty and liquidus temperature (that temperature when crystalline phases begin to form in the melt).

[d] The observations are made on glasses that were stoichiometrically compounded standard glasses; thus the assumption that all error is in the property measurement is a good one.

[e] This applies to the durability constraint since there is an upper limit on the allowable leach rate. The resulting solution is actually that to a quadratic equation providing the composition terms at both upper and lower confidence curves at the leach rate limit.

[f] Those elements that have an appreciable effect on the property in question. The composition is normalized over more than the q elements which in turn removes the unit-sum constraint from the variance derivation.

$$\frac{y\underline{\Delta}^T - \mu\underline{\Delta}^T}{\sqrt{\underline{\Delta} S \underline{\Delta}^T}}$$

is distributed as a Student's t with (m–1) degrees of freedom.[6,7] This is used to transform the necessary acceptance test into one that assures the composition is acceptable allowing for both modeling and measurement uncertainties.

C. Process Uncertainty

The final ingredient in the uncertainty picture for DWPF is the variance associated with blending the feed streams that produce the melter feed slurry in such a way as to ensure that the melt and glass product will possess acceptable properties. As illustrated in Figure 1, the radioactive Sludge and PHA are first blended and processed in the SRAT. The resulting SRAT product material is then transferred to the SME where it is blended with the glass frit slurry prior to transfer to the MFT and then the melter. The SME is the final location in DWPF whereby control can be imposed on the DWPF product. Thus there must be a high degree of certainty that the feed slurry produced in the SME will eventually result in an acceptable product.

Controlling blending in the SRAT and SME vessels is the first step to assuring that acceptable melter feed is produced. Using error propagation, the uncertainties associated with processing the prescribed SRAT and SME target blends are incorporated into the blending algorithms[g] to provide a melter feed with high confidence of acceptable durability. Similar treatments are used for the other process and product constraints. Thus the uncertainties due to modeling, sampling and measurement, and processing are managed in such a way as to assure that acceptable product is produced. Finally, the composition of the melter feed material will be monitored to assure that it satisfies the appropriate constraints. Any remedies are determined in as analogous fashion to the SRAT and SME target blends.

III. APPLICATION OF THE PCCS TO DWPF COMPOSITION CONTROL

DWPF is the nation's first and the world's largest facility to immobilize high-level nuclear waste. Construction of the facility has recently been completed, and facility start-up has commenced using non-radioactive, simulated feed material. The first two batches of melter feed have been prepared using PCCS to prescribe SRAT and SME target blends and monitor the resulting melter feed material produced in the SME.[h] Since the DWPF melter is not yet operational, crucible studies have been used to confirm that the durability of the glass produced from this melter feed will indeed be acceptable to at least the 95% confidence level. Other tests will be performed after the DWPF melter becomes operational and the melter feed is vitrified.

A. Prescription of DWPF SRAT Target Blends

The available simulated Sludge, PHA, and Frit compositions are initially entered into the PCCS and subsequently stored in the system's database. The Sludge will enter DWPF from the Tank Farm via a pump pit. The Sludge tank is designated 241H-40/51. The PHA is prepared in the DWPF Salt Processing Cell and is stored in the Precipitate Reactor Bottoms Tank (PRBT) prior to addition to the SRAT. The Frit slurry is stored in the Process Frit Slurry Feed Tank (PFSFT) prior to addition to the SME. Once these compositions are entered, the PCCS can be queried for the best blend of Sludge, PHA, and Frit to produce acceptable melter feed batch. The results of the target blend determination for the very first DWPF Chemical Run SRAT batch are shown in Figure 2.

B. Details of the PCCS Batching Data Display

The results of a SRAT or SME target blend are displayed on the PCCS Batching Data Display as illustrated in Figure 2. The upper left-hand pane of the display provides a graphical representation (i.e., ternary diagram) of the processing region available to DWPF for the compositions entered and the variances known. The regions displayed include that including all appropriate uncertainty, that defined by the modeling uncertainty, and that from which no uncertainty is included.

The pane directly beneath this representation provides information concerning the constraints that must be satisfied for the DWPF product to be both processible and acceptable. Both the limits and the required confidences are adjustable. Each of these constraints are managed in the same manner as the durability which was concentrated on in this paper. The confluence of the acceptable regions for all the constraints define the overall acceptable regions shown in Figure 2.

[g] The process uncertainty is thus added to the blend determination in such a way that the resulting blended melter feed has a 95% confidence of having acceptable durability.

[h] No remedies have been necessary during initial processing in DWPF.

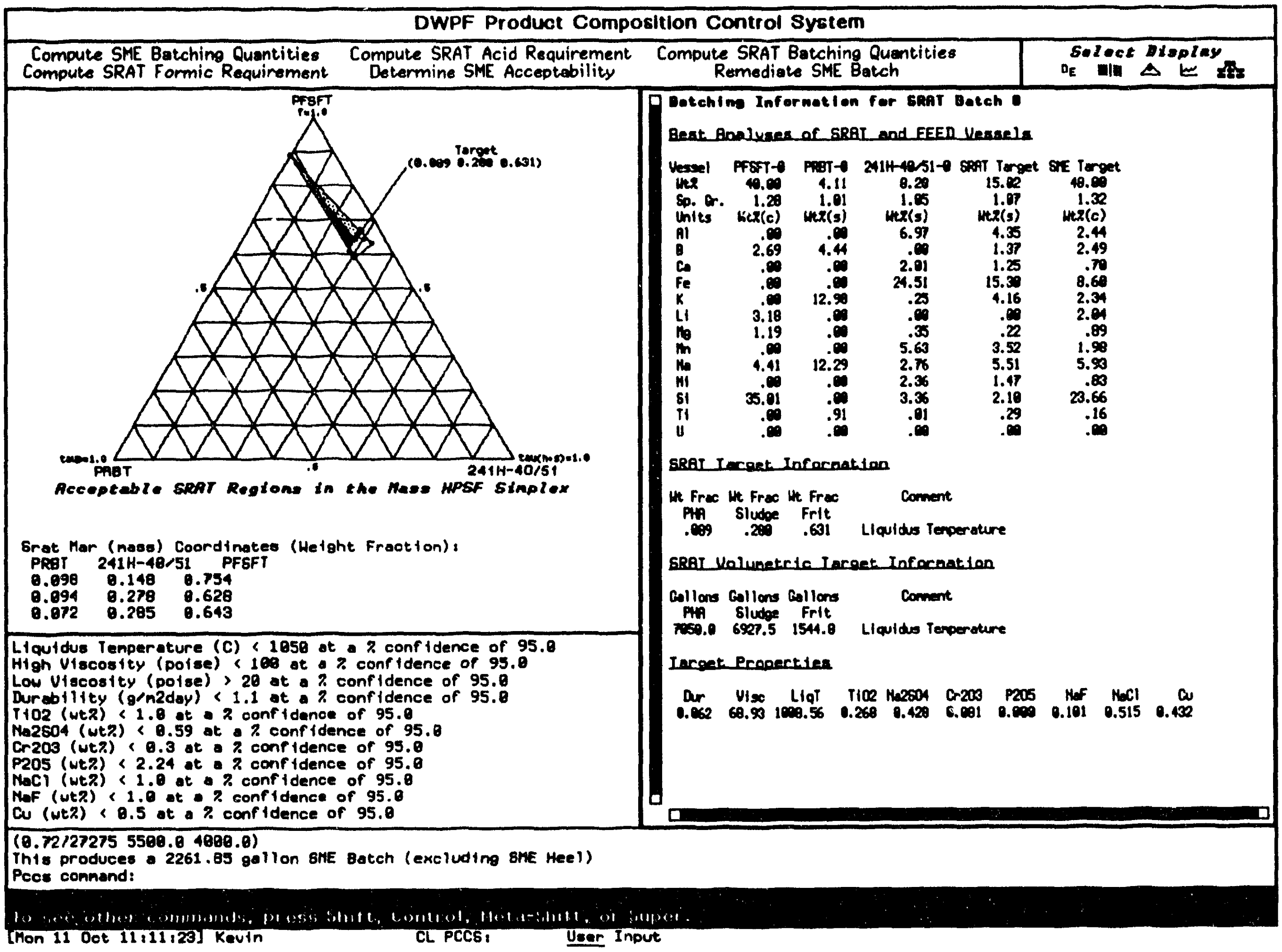

Figure 2. DWPF PCCS SRAT Batch 1 Target Blend Information

The large pane to the right provides detailed information concerning the compositions of the feed materials as well as the SRAT and SME target blend and composition information. The volumetric target blend information in Figure 2 was that used by DWPF to prepare the first SRAT batch. The frit information must be included in the target blend determination as this is the only manner in which the waste streams can be projected to glass composition.

Once the SRAT product material is produced, the PCCS is again queried to prescribe the best blend of the SRAT product and Frit slurry (with the existing SME Heel material). The results for this blend are displayed much like those in Figure 2 for the SRAT blend. The SME target blend thus computed was to prepare the first SME batch for DWPF. The composition of this melter feed material was thoroughly measured and the PCCS was used to monitor the composition for acceptability. This melter feed was deemed acceptable by PCCS and was thus ready for vitrification.

Two additional SRAT product batches and one additional SME product batch were produced during the first series of DWPF Chemical Runs. All blends were prescribed by PCCS and the melter feed material produced was monitored and deemed acceptable. This material was then compounded and sampled. Crucible studies were conducted using the compounded material since the DWPF melter is not yet operational. The results of the tests on this material show that it meets the durability criterion as predicted by PCCS. This is the most crucial constraint imposed upon the DWPF product. The other criteria will be tested after the melter feed has been vitrified in the DWPF melter.

IV. OTHER PCCS APPLICATIONS

PCCS and its blending and monitoring algorithms have been used to define target blends and remedies as well as monitor the compositions produced in a number of applications representative of DWPF. These include, 1/200the scale, crucible studies, the DWPF pilot facility operated by SRTC as well as operations in the SRTC shielded facility where actual sludge has been vitrified according to PCCS. The algorithms have even been applied to Hanford-type processing done by SRTC with acceptable results.

V. LESSONS LEARNED FROM THE APPLICATION OF SPC TO COMPOSITION CONTROL

There has been extensive testing of the PCCS and its algorithms. The results illustrate not only that the DWPF product can be controlled using PCCS; however, more importantly, it illustrates that such a process must be controlled using the rigorous, multivariate approach provided by PCCS to have any possibility of producing acceptable waste glass in an efficient, controlled manner. No commercially available packages provide the necessary statistical foundation necessary to solve the DWPF composition control problem. Diverse sources of uncertainty (e.g., sampling, preparation, and analytical) complicate the process control. DWPF product property control connotes composition control, i.e., controlling a large number of uncertain and highly correlated variables to the degree that they satisfy a myriad of constraints both process and product-related to a high degree of certainty. The PCCS represents an innovative approach to answer this control problem in a rigorous, defensible manner.

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NOMENCLATURE

a, b	fitted parameters of the property prediction model
y_i, $\underline{y}$	normalized molar oxide concentration of the i^{th} element and array of same
Δ	total molar free energy of hydration (kcal/mole)
Δ_i, $\underline{\Delta}$	component molar free energy of hydration for the i^{th} element and array of same
s_r	residual standard deviation
$F(\nu_1, \nu_2)$	F-statistic at ν_1 and ν_2 degrees of freedom
n	number of data points used to derive the property model
(X^TX)	product moment matrix
μ	true normalized molar oxide composition
Σ	true covariance matrix for μ
S	sample estimate of Σ based upon m sample observations

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