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THE PRODUCT COMPOSITION CONTROL SYSTEM AT SAVANNAH RIVER: STATISTICAL PROCESS CONTROL ALGORITHM (U)

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THE PRODUCT COMPOSITION CONTROL SYSTEM AT SAVANNAH RIVER: THE STATISTICAL PROCESS CONTROL ALGORITHM

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The Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) in Aiken, South Carolina, will be used to immobilize the 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 insoluble sludge and precipitate and less radioactive water soluble salts. (In a separate facility, the soluble salts are disposed of as low-level waste in a mixture of cement, slag, and flyash.) In DWPF, precipitate (PHA) is blended with 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 glass wasteform be resistant to leaching by underground water that might contact it.[1] In addition, there are processing constraints on melt viscosity, liquidus temperature, and waste solubility:[2,3]

Acceptability	Processability
Leach Rate ≤ 131 TDS EA Glass[1]	Liquidus Temperature ≤ 1050°C
	20 ≤ Melt Viscosity ≤ 100 poise
	TiO_2, NaF, & NaCl ≤ 1.0 wt%
	Cr_2O_3 ≤ 0.3 wt%
	SO_4^{2-} ≤ 0.4 wt%
	Cu ≤ 0.5 wt%
	PO_4^{3-} ≤ 3.0 wt%

PCCS STATISTICAL PROCESS CONTROL (SPC) ALGORITHM

<u>What Is It?</u> The Product Composition Control System (PCCS) is the amalgam of computer hardware and software intended to ensure that the melt will be processable and that the glass wasteform produced will be acceptable.

Within PCCS, the SPC Algorithm is the means which guides control of the DWPF process.

Why Is It? The SPC Algorithm is necessary to control the multivariate DWPF process in the face of uncertainties (variances and covariances) arising from the process, its feeds, sampling, modeling, and measurement systems.

What Does It Do? The SPC Algorithm:

- derives target blends (mass fractions p of PHA, s of Sludge, and f of Frit) which will combine with current SRAT (r) and SME (m) Heels to produce melter feed with desirably high waste-loading,

- monitors extant SME batches for melt processability and product acceptability prior to clearing them for transfer to the Melter Feed Tank (MFT) where they will be fed to the DWPF melter,

- and finally determines remedies from a predefined set of trim chemicals and frit slurry to correct unacceptable SME batches

in such a way that the resulting melts will very likely process into good product. The particulars of the DWPF process as they relate to PCCS are illustrated in Figure 1; however, for simplicity, the discussion here will be limited to melter feed slurry monitoring.

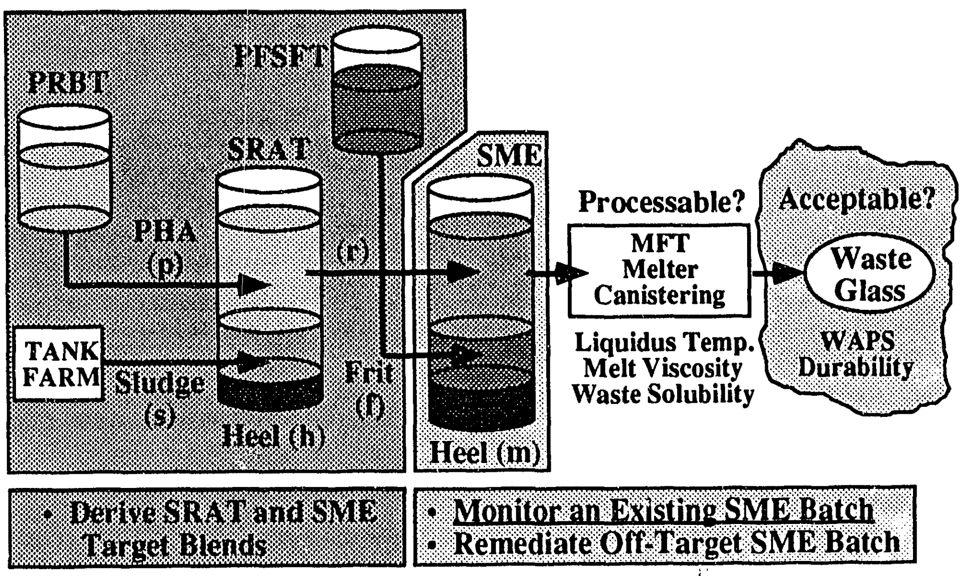

Figure 1. The Product Composition Control System and DWPF

When monitoring the SME composition, the PCCS SPC Algorithm considers:

- uncertainties in slurry sampling, sample preparation and chemical analysis;
- uncertainty in prediction of properties from slurry composition;
- simultaneous variation of the individual constituent concentrations;
- mass balance information to augment the measurement data;
- and the Waste Acceptance Preliminary Specifications (WAPS).[1]

It will also take into account process and input feed variations as they become better characterized during operation.

CHARACTERIZING DWPF PRIOR TO MAKING PRODUCT

The properties that must be controlled (e.g., durability) cannot be measured in situ. Furthermore, the material in the DWPF melter cannot be adjusted; the SME is the last vessel in which the material can be easily altered. (See Figure 1.) Therefore, the important glass and melt properties have been related to glass (and feed) composition which can be measured directly and thus controlled. Both glass chemistry theory and empirical least-squares fitting show that straight-line regressions relate these properties to unique, rational functions of the composition. For example, the durability (or, in this case, the log of the leach rate of Si) is related to molar oxide composition by:

$$\log \mathrm{Si}\ (\mathrm{g/m^2}) = 0.4528 - 0.1638\ \Delta G_{hyd}(\mathrm{kcal/mol})$$

where†

$$\begin{aligned}\Delta G_{hyd} = {} & 15.5[Fe_2O_3] + 5.59[SiO_2] + 3.04[Al_2O_3] - 52.915[K_2O] \\ & - 28.33[Li_2O] - 34.405[Na_2O] - 9.93\,[B_2O_3] - 19.937[NiO] \\ & - 21.706[CaO] - 20.461[MnO] + 15.99[TiO_2] - 19.478[MgO].\end{aligned}$$

To characterize the process prior to making and inspecting either the melt or product, the properties are predicted from measured feed slurry composition using their respective straight-line regressions. Each regression equation can be back-solved to provide the value corresponding to its property limit (e.g., ΔG_{hyd} for durability); this transforms the constraint on that property into an

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†Additional elements are included in the ΔG_{hyd} computation if they will be present in the glass product in appreciable amounts.

equivalent constraint on molar oxide composition.

The Leach Rate of waste glass produced in DWPF must be demonstrably less than that of an accepted standard glass designated as 131 TDS EA.[1] The Leach Rate of this glass is approximately 1 g/m^2/day over 28-day period using an MCC-1 type leach test.[4] Thus, the Leach Rate must satisfy ($\log Si \leq \log(28)$) for the 28 day testing period. This transforms into ($\Delta G_{hyd} \geq -6.07$ kcal/mol) as illustrated in Figure 2.

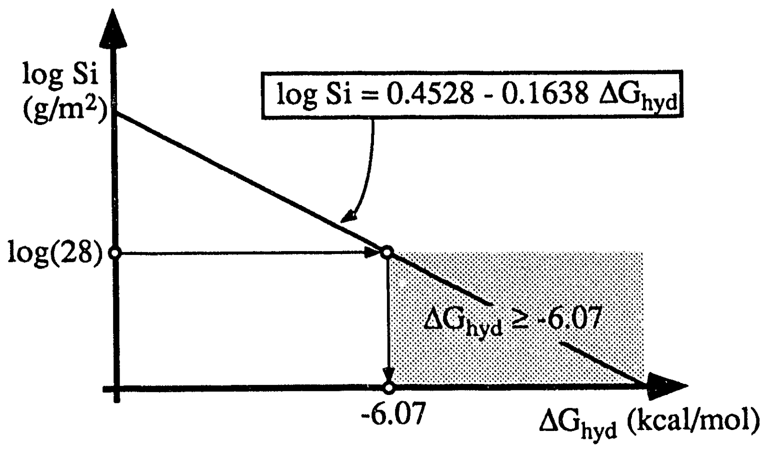

Figure 2. The Durability Correlation

Thus the durability property limit translates into the following inequality on the molar oxide composition:

$$\{\Delta G_{hyd} = 15.5[Fe_2O_3] + 5.59[SiO_2] + \ldots - 19.478[MgO]\} \geq \{-6.07\}$$

or in vector notation:

$$[\underline{x}_d]\,[\underline{\alpha}_d]' \geq -6.07 \text{ kcal/mol}$$

where: $[\underline{x}_d] =$ $[[Fe_2O_3], [SiO_2], [Al_2O_3], [K_2O], [Li_2O], [Na_2O], [B_2O_3], [NiO], [CaO], [MnO], [TiO_2], [MgO]]$

and: $[\underline{\alpha}_d] =$ [15.5, 5.59, 3.04, -52.915, -28.33, -34.405, -9.93, -19.937, -21.706, -20.461, 15.99, -19.478].

The inequality thus formed describes a region in molar composition space (i.e., $\underline{x}$-Space), the locus of points which provides predicted values of the leach rate that are acceptable (i.e., greater than -6.07 kcal/mol). This region is denoted as the Expected Property Acceptable Region or EPAR. There are corresponding cases for the other property constraints. Figure 3 illustrates the EPAR for Durability in 2 dimensions. For illustration, the iron and silicon oxides are selected as the two elements, and all others are fixed (as represented by an *). Thus,

$$\{15.5[Fe_2O_3] + 5.59[SiO_2] + A\} \geq -6.07$$

$$\text{where } A = 3.04[Al_2O_3]^* - 52.915[K_2O]^* - \ldots - 19.478[MgO]^*$$

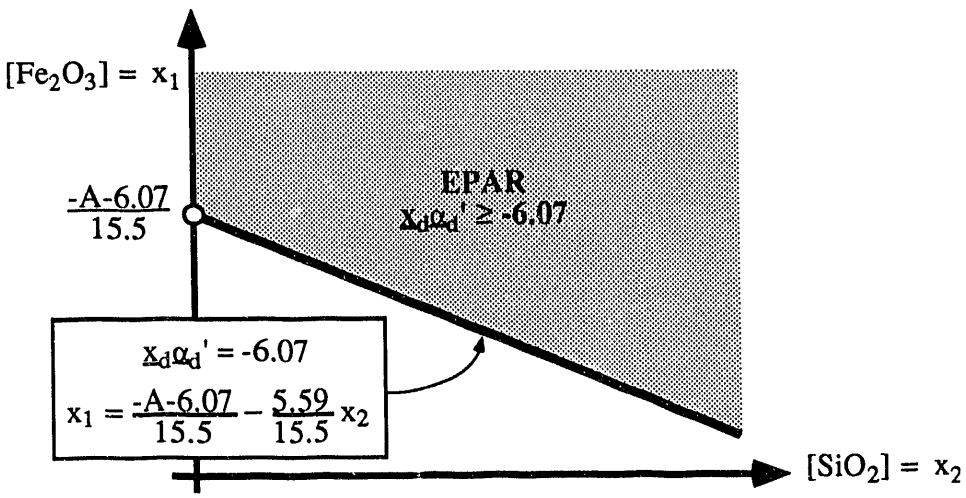

Figure 3. The Durability EPAR in 2 Dimensions

ACCOUNTING FOR PREDICTION UNCERTAINTY

To monitor an already blended SME batch, the Algorithm first accounts for the (random) uncertainty of prediction through use of Scheffé simultaneous confidence bands[5,6] around the straight-line regressions. For durability, these confidence bands are described by:

$$\text{Model Value} \pm s_r\sqrt{qF(q,n-q)}\sqrt{\underline{z}_0(X'X)^{-1}\underline{z}_0'} \quad \text{where } \underline{z} = [1, \Delta G_{hyd}].$$

These bands utilize the estimate of the random error standard deviation (s_r), the design of the parent data $(X'X)^{-1}$, and the F-statistic to provide at any $\Delta G_{hyd} = (\Delta G_{hyd})_0$ confidence limits on the model value which hold simultaneously for all ΔG_{hyd}. They are thus appropriate for repeated use of the regression line.

The appropriate (upper or lower) confidence band is back-solved for a new limit on ΔG_{hyd}, ΔG_{hyd}^*, corresponding to the acceptable property limit. This procedure produces an inequality like that which generated the EPAR for durability. (See Figure 3.) The boundary of this new inequality is a constraint hyperplane in molar composition space (i.e., x-space) which accommodates the random uncertainty in model predictions. The region formed by the new inequality, the Property Acceptable Region (PAR), is the locus of all compositions which provide acceptable predicted properties even allowing for the random uncertainty in the model. The PAR is interior to (and thus more conservative than) the EPAR. Figure 4 illustrates this procedure for durability.

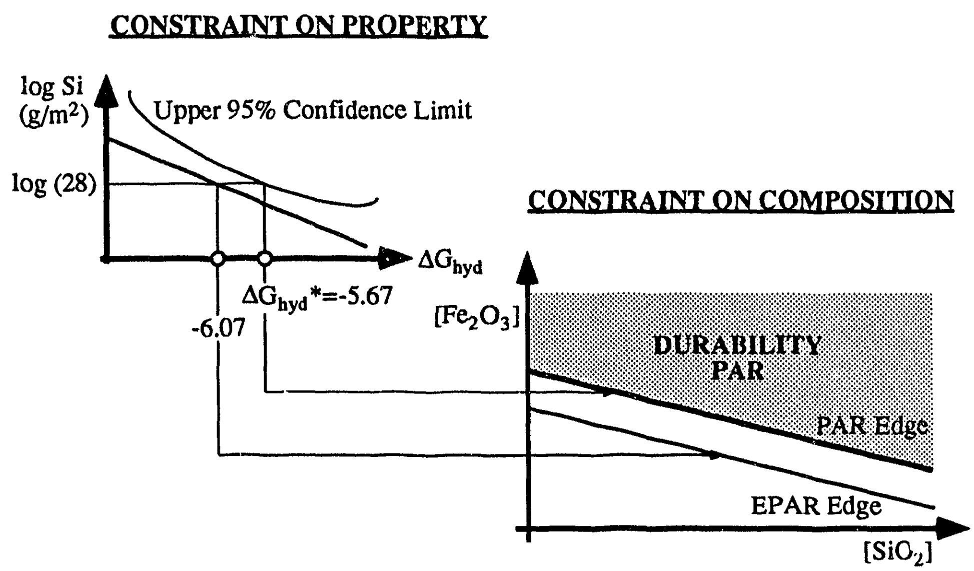

Figure 4. Durability Property Acceptability and PAR

There is a separate PAR for each property. The confluence of these PAR's forms the overall PAR. Any point located within the overall PAR represents a measured SME batch composition which will give predicted properties that meet all the stated limits, even allowing for modeling uncertainty. The overall PAR is illustrated in Figure 5.

ACCOUNTING FOR MEASUREMENT UNCERTAINTY

Thus far, only the uncertainties arising from the original measurements used to derive the property correlations have been addressed. The glasses used to develop the property correlations were either standard or stoichiometrically-compounded. Thus the compositions for the glasses from which the property models were derived were assumed known; however, during DWPF operation, the compositions from which these properties must be estimated will not be known, only measured. There will be appreciable errors in composition arising from the DWPF sampling and measurement systems; therefore, these errors must be addressed.

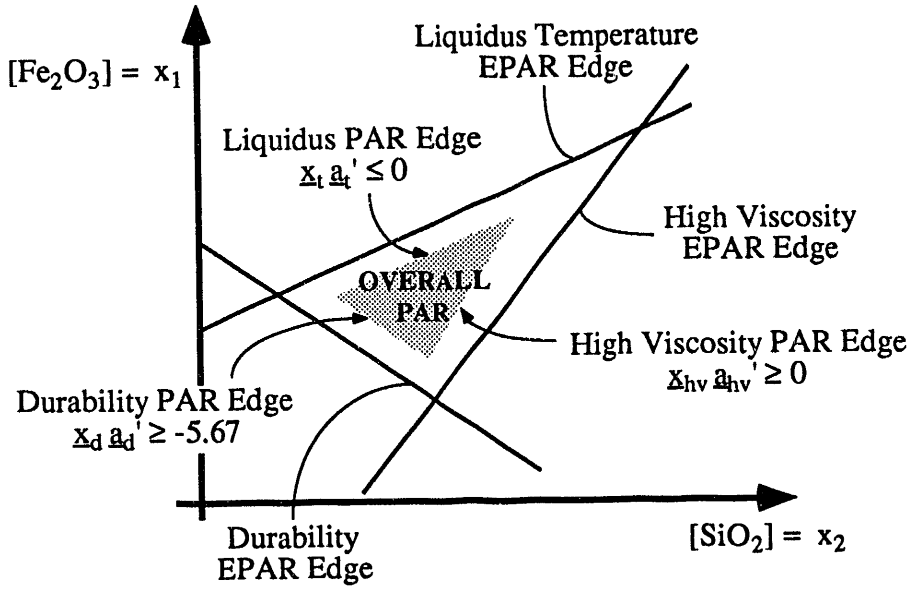

Figure 5. The DWPF Overall Property Acceptable Region (PAR)

A SME composition measurement, $\underline{x}_m$, is a q dimensional vector of simultaneous measurements on q constituent oxides:

$$\underline{x}_m = [[Fe_2O_3], [SiO_2], \ldots, [MgO]] = [x_1, x_2, \ldots, x_q].$$

Therefore, the description of the uncertainty in $\underline{x}_m$ requires the use of multivariate statistical techniques.† If the concentrations of the individual constituents can be assumed multivariate Gaussian, then traditional methods of multivariate normal theory apply.

S_M is the covariance matrix based on the historic sampling of several such measurements (not including $\underline{x}_m$). S_M consists of the variances within and covariances between the "q" individual constituents:

†A more simplistic alternative, that of applying several sets of univariate control limits independently, is theoretically and pragmatically counterproductive since it causes the false-reject rate to sky-rocket. If there are q=10 constituents to be controlled, and if 95% control limits are applied independently on each, from probability considerations alone some 40% of the candidate feed batches will be rejected even though they are good feed material.

$$S_M = \begin{bmatrix} s_{11} & s_{12} & \cdots & s_{1q} \\ s_{12} & s_{22} & \cdots & s_{2q} \\ \cdots & \cdots & \cdots & \cdots \\ s_{1q} & s_{2q} & \cdots & s_{qq} \end{bmatrix}$$

where the s_{ij} are the sample variances (i=j) and covariances (i≠j):

$$s_{ij} = \frac{1}{n-1} \Sigma(x_{ik} - \overline{x}_i)(x_{jk} - \overline{x}_j)$$

$$\overline{x}_j = \frac{1}{n} \Sigma x_{jk} \qquad k = 1, 2, \ldots, n.$$

Suppose the measurement $\underline{x}_m$ is distributed as multivariate Gaussian around its true mean $\underline{\mu}$ with covariance Σ_M. This implies that the linear combination $\underline{x}_m\underline{a}'$ is distributed as univariate Gaussian with mean $\underline{\mu}\,\underline{a}'$ and variance $\underline{a}S_M\underline{a}'$.[7] A further result is that the quantity

$$\frac{\underline{x}_m\underline{a}' - \underline{\mu}\,\underline{a}'}{\sqrt{\underline{a}S_M\underline{a}'}}$$

is distributed as a Student's t with (m-1) degrees of freedom; S_M is the previous sample estimate of Σ_M based on m historic observations.[8]

The requisite tests that must be satisfied for measurement acceptability are of the form: $\underline{\mu}\,\underline{a}' \geq \varepsilon$ or $\underline{\mu}\,\underline{a}' \leq -\varepsilon$, depending on the type of test. For durability, this implies that the measured composition must satisfy:

$$(\underline{x}_m\underline{a}' + 5.67) \geq t_{0.95}(m-1)\sqrt{\underline{a}S_M\underline{a}'}.$$

There are corresponding tests for the other constraints. If the composition satisfies all these tests, the SME batch is adjudged to be measurement acceptable.

MONITORING A SME BATCH

The comparison of the form $(\underline{x}_m\underline{a}' + \varepsilon_0) : \pm\, t_{0.95}(m-1)\sqrt{\underline{a}S_M\underline{a}'}$ determines whether a blended SME batch composition is measurement acceptable for a given property. Using durability as an example,

> If $(\underline{x}_m\underline{a}' + 5.67) \geq t_{0.95}(m-1)\sqrt{\underline{a}S_M\underline{a}'}$, then $\underline{x}_m$ is statistically distinguishable (at the 95% confidence level) from the durability PAR edge, and the SME batch is measurement acceptable for durability.

If $(\underline{x}_m\underline{a}' + 5.67) < t_{0.95}(m-1)\sqrt{\underline{a}S_M\underline{a}'}$, then $\underline{x}_m$ is not statistically distinguishable (at the 95% confidence level) from the durability PAR edge, and the SME batch is not measurement acceptable for durability.

The Measurement Acceptable Region in molar composition space (i.e., the $\underline{x}$-MAR) is that region containing all compositions which are measurement acceptable. To bound potential target blends, the edges of the $\underline{x}$-MAR are determined by using the t-test. Marginal durability measurement acceptability occurs at: $(\underline{x}_m\underline{a}' + 5.67) = t_{0.95}(m-1)\sqrt{\underline{a}S_M\underline{a}'}$. Since $\sqrt{\underline{a}S_M\underline{a}'}$ is the propagated standard error of $\underline{x}_m\underline{a}'$, the right-hand side of this equality represents the minimum distance (expressed as the number of standard errors) $\underline{x}_m$ must be away from the PAR edge, $(\underline{x}\,\underline{a}' + 5.67) = 0$, to be measurement acceptable.

The vector-matrix products in the t-tests above ($\underline{x}_m\underline{a}'$ and $\underline{a}S_M\underline{a}'$) are scalars, so the test collapses the q-dimensional geometry of molar composition space to a single dimension for decision making. Since the standard error, $\sqrt{\underline{a}S_M\underline{a}'}$, does not change with composition for a SME batch, the MAR edge is a constant distance, t(m-1) standard errors, away from the PAR edge for all SME blends in $\underline{x}$-space. The MAR edge will thus be a hyperplane parallel to the PAR edge. That hyperplane is the closest a measurement can get to the PAR edge and yet still be measurement acceptable. Figure 6 illustrates the geometry of the Durability $\underline{x}$-MAR for extant SME batches. There are similar $\underline{x}$-MAR's for the other property constraints, and the confluence of these hyperplanes form the boundary of the overall MAR in composition space. This region will be entirely interior to the overall PAR illustrated in Figure 5.

INCORPORATING PROCESS INFORMATION

To improve the precision of the measurements, the Algorithm augments the measurement information available for process control by incorporating all other relevant process information into the measurement system through use of a Maximum A Posteriori (MAP) estimator.[9] The MAP estimator uses a state model projection for the SME composition after receipt of the SRAT material and addition of frit slurry but prior to the control laboratory measurement:

$$\begin{bmatrix}\text{SME State}\\ \text{Model}\\ \text{Projection}\end{bmatrix} = \frac{1}{2}\begin{bmatrix}\text{Elemental} & & \text{Elemental}\\ \text{Masses} & + & \text{Masses}\\ \text{Leaving SRAT} & & \text{Entering SME}\end{bmatrix} + \begin{bmatrix}\text{SME}\\ \text{Heel}\\ \text{Composition}\end{bmatrix}$$

The MAP composition estimate is the following linear combination of this state model projection and relevant laboratory measurement:

$$\begin{bmatrix}\text{SME MAP}\\ \text{Estimate}\end{bmatrix} = \begin{bmatrix}\text{State}\\ \text{Projection}\end{bmatrix} + \mathbf{K}\begin{bmatrix}\text{Laboratory}\\ \text{Measurement}\end{bmatrix} - \begin{bmatrix}\text{State}\\ \text{Projection}\end{bmatrix}$$

where the "MAP Gain" **K** results from balancing the uncertainty in the state model projection against that of the measurement. In scalar applications, **K** ranges over the unit interval (0,1).

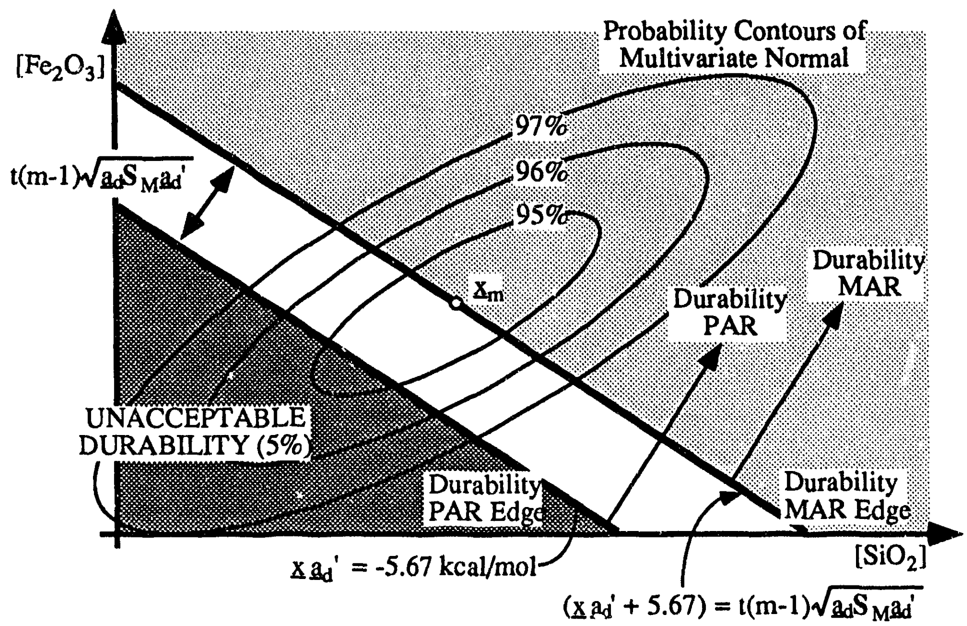

Figure 6. Geometry of the Durability MAR

ADVANTAGES OF THE ALGORITHM

By accommodating the multivariate aspects of the composition measurement system and by incorporating the uncertainty of the property models, the PCCS correctly maintains the false-alarm rate (proportion of good SME batches wrongly judged to need remediation). By incorporating mass transfer measurements into the control algorithm, it increases the useful information and, in so doing, relieves some of the stress on the analytical laboratory. The built-in redundancy of the mass transfer measurements with the composition measurements also provides a means of detecting aberrations in either.

By devising target blends to provide acceptable properties, it smooths out batch-wise differences in feed composition to give an "on-aim" type of control scheme on properties rather than a "within-limits" type of control on composition (hence, the Statistical Process Control Algorithm).

The PCCS has been used to guide research and develop operating procedures for DWPF. It has also been used to control operations in both the DWPF pilot facility and the Shielded Cells Facility at the Savannah River Technology Center where actual DWPF sludge has been processed into acceptable glass. Thus the PCCS has proven to be an invaluable tool in the development of the DWPF process control strategy.

There has been extensive testing of the PCCS by both the developers and DWPF Technical personnel. DWPF Technical personnel have accepted the PCCS for use in guiding control of DWPF for Startup and Radioactive Operations. The PCCS will allow DWPF to be operated in an efficient, consistent, and controlled manner.

There are no commercially available packages that furnish solutions to the problems addressed by the PCCS. Divers variance sources (e.g., sampling, modeling, analytical, and process-related) complicate process control. Controlling the DWPF connotes controlling a large number of noisy and often highly correlated constituent concentrations that must be shown to meet many constraints (e.g., waste glass durability) to a high degree of certainty. The algorithms comprising the PCCS are innovative because they provide a rigorous, statistically-defensible management of a noisy, multivariate system with multiple constraints imposed.

ACKNOWLEDGMENTS

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