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DWPF WASTE GLASS PRODUCT COMPOSITION CONTROL SYSTEM (U)

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INTRODUCTION

The Defense Waste Processing Facility (DWPF) will be used to blend aqueous radwaste (PHA) with solid radwaste (Sludge) in a waste receipt vessel (the SRAT). The resulting SRAT material is transferred to the the SME and there blended with ground glass (Frit) to produce a batch of melter feed slurry. The SME material is passed to a hold tank (the MFT) which is used to continuously feed the DWPF melter. The melter produces a molten glass wasteform 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. In addition, there are processing constraints on Viscosity, Liquidus Temperature, and Waste Solubility of the melt:

Acceptability	Processibility
Leach Rate ≤ 131 TDS EA Glass	Liquidus Temperature ≤ 1050°C
	$20 \leq$ Melt Viscosity ≤ 100 poise
	TiO_2, NaF, & NaCl ≤ 1.0 wt% (in glass)
	Cr_2O_3 & Cu ≤ 0.3 wt% (in glass)
	$SO_4 \leq 0.4$ wt% (in glass)
	$PO_4 \leq 3.0$ wt% (in glass)

THE PCCS STATISTICAL PROCESS CONTROL (SPC) ALGORITHM

<u>What Is It?</u> The Product Composition Control System (PCCS) is the system intended to ensure that the *melt will be processible* and that the *glass wasteform will be acceptable*. Within the PCCS, the SPC Algorithm is the means which *guides control of the DWPF process.*

<u>Why Is It?</u> The SPC Algorithm is needed to control the *multivariate* DWPF process *in the face of uncertainties (variances and covariances)* which arise from the process, its feeds, sampling, modeling, and measurement systems.

<u>What Does It Do?</u> 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 a SME batch with desirably high waste-loading,

- *monitors a pending SME batch* composition for melt processibility and product acceptability prior to clearing it for transfer to the MFT,
- and *derives a remediation blend* of trim chemicals and frit to correct an unacceptable SME batch

in such a way that *the resulting melt will likely process into good product.* The essentials of the DWPF Process and the PCCS are illustrated in Figure 1; however, for simplicity we limit the discussion here to *monitoring.*

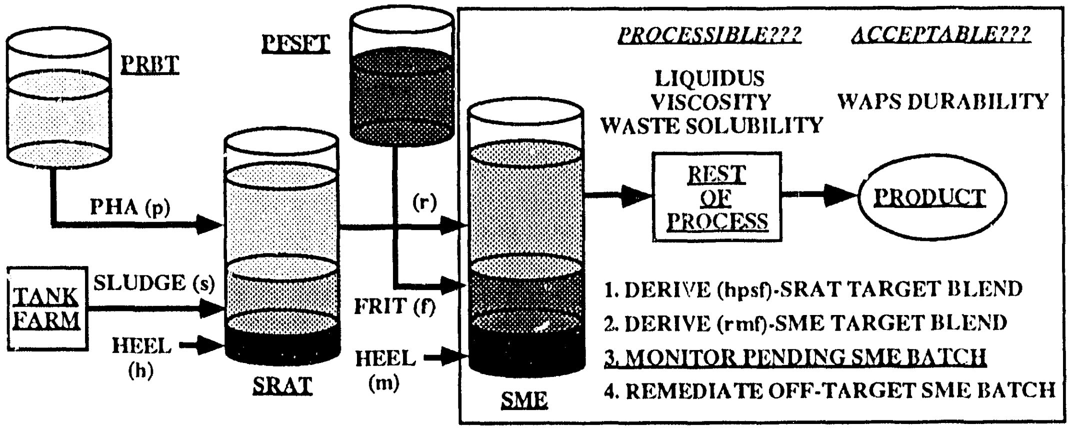

Figure 1 The Product Composition Control System and DWPF

To monitor the SME batch composition, the PCCS SPC algorithm takes into account:

- uncertainties in slurry *sampling*, sample *preparation* and *measurement*;
- 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 criteria* (WAPS).

It will take into account *process and input feed variations* as they become known during operation.

CHARACTERIZING THE PROCESS PRIOR TO MAKING PRODUCT

The process is characterized prior to making product *by relating glass and melt properties to feed slurry composition.* The composition is expressed through a hybrid combination of elements denoted ξ. Each property has its own unique ξ. Both glass chemistry theory and empirical least-squares fitting show that *straight-line regressions* relate the glass property (Leach Rate) and the process melt properties (Viscosity and Liquidus Temperature) to the ξ's. Thus, to characterize the process *prior to making and inspecting either the melt or product*, these properties are *predicted* from measured feed slurry composition using straight-line regressions in ξ. Back-solving any such regression line to get the ξ-value corresponding to its property limit transforms the constraint on that property into an equivalent constraint on its ξ. This constraint on ξ, in turn, becomes a constraint on the concentrations of the individual constituent oxides (the "x_i's"). For example,

the Liquidus regression is: $T_L = 803.8698 + 2276.8724\xi_t$

and its ξ is: $\xi_t = \dfrac{134[Fe_2O_3]}{156[SiO_2] - 360[Al_2O_3]}$.

Its property limit is: $T_L \le 1050°C$

which transforms to: $\xi_t \le \left[\underline{0.108} = \dfrac{1050 - 803.8698}{2276.8724}\right]$.

Graphically, this is illustrated in Figure 2.

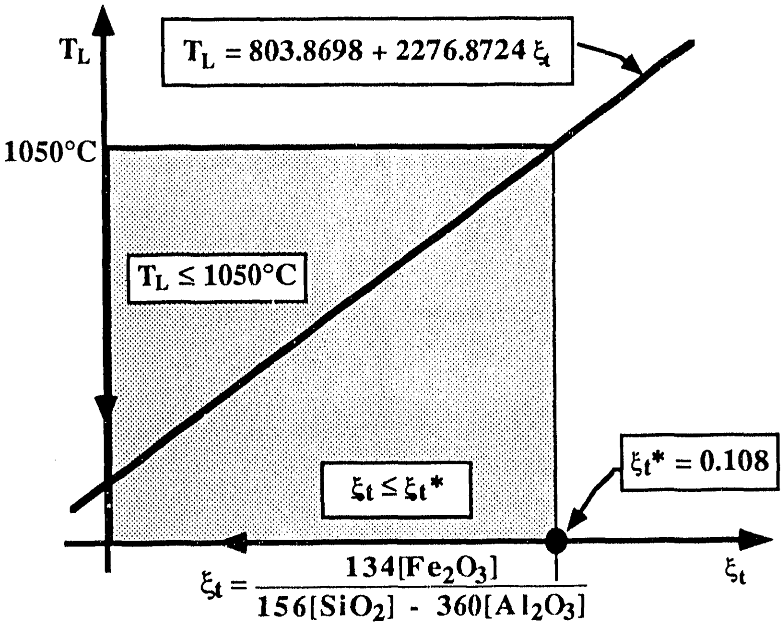

Figure 2 Liquidus Correlation

Thus, $T_L \le 1050°C$ becomes: $134[Fe_2O_3] \le 0.108\big(156[SiO_2] - 360[Al_2O_3]\big)$

or: $\big(134[Fe_2O_3] - 16.848[SiO_2] + 38.88[Al_2O_3]\big) \le 0$

or: $[\underline{x}_t]\,[\underline{\alpha}_t]' \le 0$

where: $[\underline{x}_t] = ([Fe_2O_3],[SiO_2],[Al_2O_3])$ and $[\underline{\alpha}_t] = [134, -16.848, 38.88]$.

The inequality thus formed determines a region in measured composition space ($\underline{x}$-Space), all points of which give predicted values of T_L that are Acceptable (i.e., $\le$ 1050°C). Denote this region the *Expected Property Acceptable Region (EPAR)*. Figure 3 illustrates the EPAR for Liquidus (using only 2-dimensions for clarity).

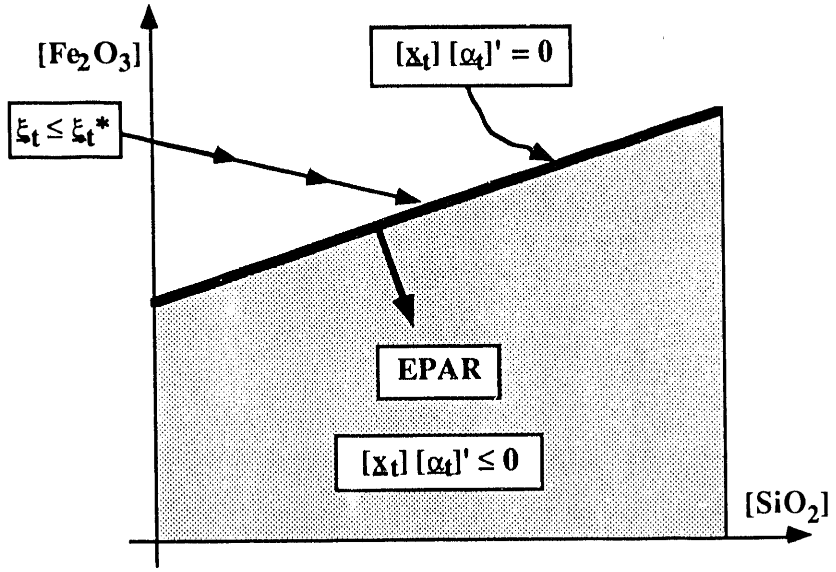

Figure 3 Liquidus EPAR in 2 Dimensions

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*[1] around the straight-line regressions:

Scheffe-type Bands: $$\text{Model Value} \pm s_r\sqrt{q\,F(q,n-q)}\sqrt{\xi_0\,(X'X)^{-1}\,\xi_0'}$$

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 $\xi = \xi_0$ confidence limits on the model value which hold simultaneously for all ξ. They are appropriate for *repeated* use of the line.

Back-solving the appropriate (upper and/or lower) *confidence band* for a new ξ-limit, ξ^*, corresponding to the acceptable property limit produces other inequalities like those which generated the EPAR. These new inequalities are *constraint hyperplanes* in x-Space which accommodate the random uncertainty in the predictions. Call them Constraint Uncertainty Planes and denote them as *x-CUP's*. These new inequalities generate the *Property Acceptable Region (PAR)*, the locus of all compositions which give acceptable property predictions even *allowing for the random uncertainty of prediction*. The PAR is interior to (and thus everywhere more conservative than) the EPAR. See Figure 4 for illustration for Liquidus. (There are corresponding but different cases for the other constraints.)

There is a separate PAR for each property. The confluence of all such PAR's forms the *overall PAR*. (Actually, only a subset will determine the overall PAR since only one of the Low Viscosity and High Viscosity constraint pair will apply to a particular case.) *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 predictive uncertainty.* The PAR is illustrated in Figure 5.

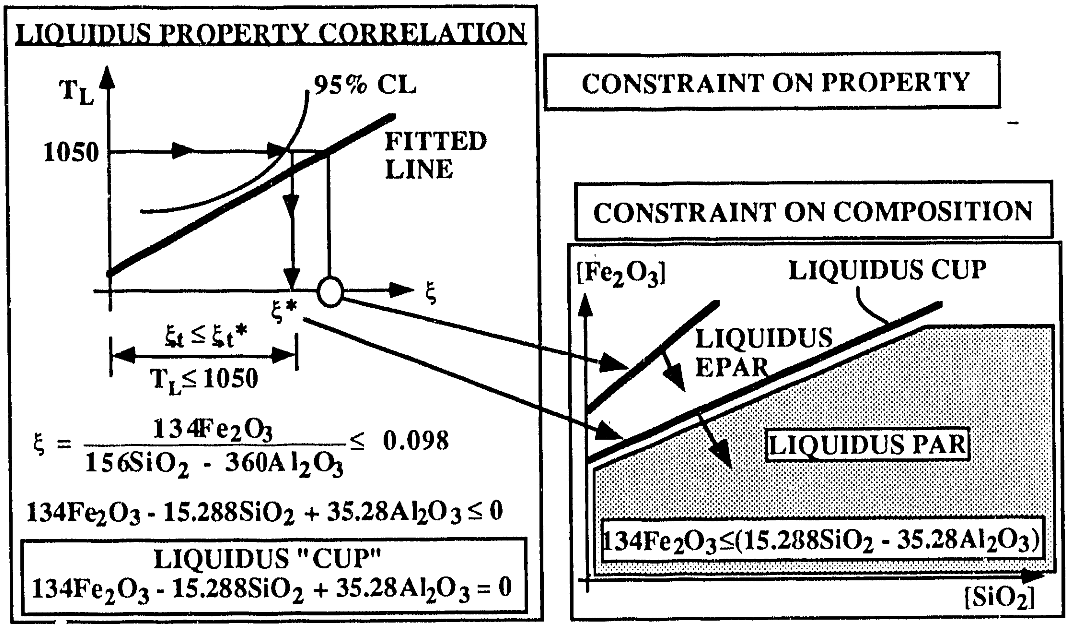

Figure 4 Liquidus Property Acceptability

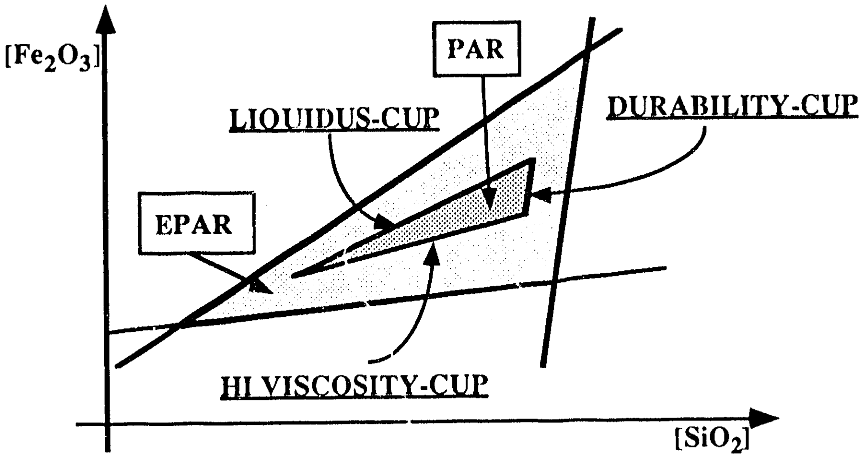

Figure 5 The DWPF Property Acceptable Region (PAR)

ACCOUNTING FOR SAMPLING & MEASUREMENT UNCERTAINTY

The PAR accommodates the random uncertainty inherent in property prediction arising from uncertainty only in the properties themselves. But, in operation, the composition of the feed slurry will not be measured to the same accuracy and precision as that of the standard glasses on which the predicting relations are based. Thus, *there will be appreciable errors in ξ*. It remains to deal with this component of uncertainty *from the sampling and measurement systems which produce the composition measurement.*

A current SME batch composition measurement $\underline{x}^m$ is a 1xq row-vector of measurements on *several constituent oxides simultaneously* : $\underline{x}^m = ([Fe_2O_3], [SiO_2], \ldots, [MgO]) = [x_1, x_2, \ldots, x_q]$.

To describe its uncertainty thus necessitates use of *multivariate* statistical techniques.[†] If 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 an historic sample of several such measurements (but not including $\underline{x}^m$). S_M consists of the variances within and covariances between the "q" individual constituents:

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

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

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

$$\underline{x}_j = \frac{1}{n}\sum x_{j\,k} \qquad k = 1,2,\ldots,n.$$

Suppose the measurement $\underline{x}^m$ is distributed in probability 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 $\underline{a}S_M\underline{a}'$.[2] A further result is that the quantity $(\underline{x}^m\underline{a}' - \underline{\mu}\underline{a}')/\sqrt{(\underline{a}S_M\underline{a}')}$ is distributed as a Student's t with m-1 degrees of freedom, where S_M is the previous sample estimate of Σ_M based on "m" historic observations.[3]

The requisite nulls which must be satisfied for measurement acceptability are of the form: $\mu a' \geq \varepsilon$ or $\mu a' \leq -\varepsilon$, depending on the type of test. For Liquidus, this implies that the composition must satisfy: $\underline{x}^m\underline{a}' \leq -t_{0.95}(m-1)\sqrt{(\underline{a}S_M\underline{a}')}$. There are corresponding tests for the other constraints. If the composition satisfies all these tests, the SME batch is adjudged measurement acceptable.

MONITORING A SME BATCH

The comparison $(\underline{x}^m\underline{a}') : \pm t_{0.95}(m-1)\sqrt{(\underline{a}S_M\underline{a}')}$ determines whether a blended SME batch $\underline{x}$ is Measurement Acceptable (MA) for a given property. Using Liquidus as an example,

> If $\underline{x}^m\underline{a}' \leq -t_{0.95}(m-1)\sqrt{(\underline{a}S_M\underline{a}')}$, then $\underline{x}^m$ *is* statistically distinguishable (at the 95% confidence level) from the Liquidus $\underline{x}$-CUP, and the SME batch *is* **MA** for Liquidus Temperature.

[†] 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.

> If $\underline{x}^m\underline{a}' > -t_{0.95}(m-1)\sqrt{(\underline{a}S_M\underline{a}')}$, then $\underline{x}^m$ *is not* statistically distinguishable (at the 95% confidence level) from the Liquidus $\underline{x}$-CUP, and the SME batch *is not* MA for Liquidus Temperature.

Define the composition-space Measurement Acceptable Region (or $\underline{x}$-MAR) to be that region containing all compositions which are MA. To bound potential target blends, determine the edges of the $\underline{x}$-MAR by using the t-test in a slightly different way. Marginal Liquidus MA occurs at the equality: $\underline{x}^m\underline{a}' = -t_{0.95}(m-1)\sqrt{(\underline{a}S_M\underline{a}')}$. Since $\sqrt{(\underline{a}S_M\underline{a}')}$ is the propagated standard error of $\underline{x}^m\underline{a}'$, the RHS of this equality represents the minimal distance (expressed as the number of standard errors) $\underline{x}^m$ must be away from the $\underline{x}$-CUP, $\underline{x}\underline{a}' + \varepsilon = 0$, to be MA.

The vector-matrix products in the t-tests above ($\underline{x}^m\underline{a}'$ and $\underline{a}S_M\underline{a}'$) are all scalars, so the test collapses the q-dimensional geometry of $\underline{x}$-space into one 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 $\underline{x}$-CUP for all SME blends in $\underline{x}$-space. The MAR edge will thus be a hyperplane parallel to the $\underline{x}$-CUP. That plane is the closest a measurement can get to the $\underline{x}$-CUP and yet still be MA. Figure 6 illustrates the geometry of the Liquidus $\underline{x}$-MAR for extant SME batches.

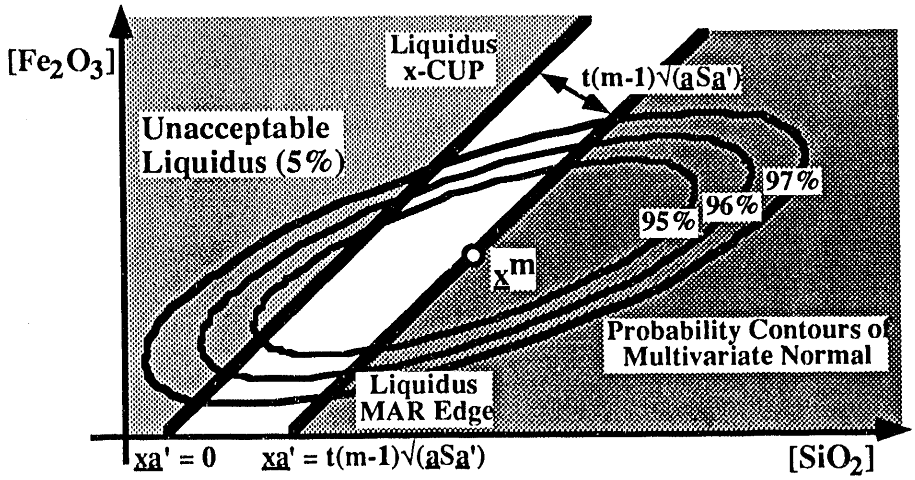

Figure 6 Geometry of the Liquidus MAR

INCORPORATING OTHER PROCESS INFORMATION

In order to improve the precision of the measurements, the algorithm augments the measurement information available for process control by incorporating other relevant process information into the measurement system through use of a *Maximum A Posteriori (MAP)*[4] *estimator.* The MAP estimator uses the *state model projection* for the SME composition after receipt of the SRAT transfer but prior to the control laboratory measurement:

[State Projection] = [Mass out of SRAT+Mass into SME]/2 + [SME Heel]

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

[SME State Estimate] = [State Projection] + **K**[Lab Measurement - State Projection]

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).

ADVANTAGES OF THE ALGORITHM

By correctly accommodating the multivariate uncertainty of the composition measurement system, and by incorporating the uncertainty of property prediction, it *correctly maintains the false-alarm rate* (proportion of good SME batches wrongly judged to need remediation) at a reasonable level.

By incorporating mass transfer measurements into the composition measurement system, it *increases the useful information* and thus relieves some of the stress on the composition measurements. The built-in redundancy of the mass transfer measurements with the composition measurements also provides a means of *detecting aberrations ("outliers")* in either.

By devising a target blend to give acceptable properties, it *smooths out batchwise 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. In so doing, it has the effect of constructing a Property "Macro-Batch" out of possibly variable input feed material.

Its quantification of process control enables DWPF *to take quantitative credit for the control efforts upstream of the MFT*; thereby relegating the MFT sample measurements to a "confirmatory" rather than a "determining" role. This translates into fewer MFT samples and less MFT measurements for equal confidence.

Expressed another way: without such an algorithm, the pre-MFT prior model is a "total ignorance" prior; namely, that the feed slurry arrives at the MFT *at random*. In that case, all the load of Waste Qualification falls on the MFT samples and measurements.

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