1 of 1

DOE/NE/44139-70

**Glass Mixing Theory and Tracer Study Results
From the SF-10 Run**

Topical Report

By

Bradley W. Bowman
Kenneth R. Routt

August 1988

Work Performed Under Contract No. DE-AC07-81NE 44139

Reported by
West Valley Nuclear Services Co., Inc.
P. O. Box 191
West Valley, New York 14171-0191

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ps

ABSTRACT

A general, partial differential equation governing glass mixing in the SFCM was derived and a solution obtained based upon certain simplifying assumptions. Tracer studies were then conducted in the SFCM during the SF-10 run to test the theory and characterize glass mixing in this melter. Analysis of the tracer data shows that glass mixing in the SFCM can be explained by use of a model of two, well-mixed tanks in series.

Table of Contents

	Acknowledgments	1
1.0	Introduction	2
2.0	Criteria for the Selection of a Suitable Tracer	3
3.0	Initial Testing for the Selection and Evaluation of Suitable Tracers	4
4.0	Development of the General Conservation of Mass Equation	10
5.0	Solution of the Conservation of Mass Equation for a Well-Mixed Tank	14
6.0	Comparison of the BaO Tracer Data to a Single, Well-Mixed Tank Model	22
7.0	Comparison of the BaO Tracer Data to a Two, Well-Mixed Tanks in Series Model	41
8.0	Comparison of the SrO Tracer Data to the Two, Well-Mixed Tanks in Series Model	48
9.0	Effect of a Growing Feed Pile	54
10.0	Residence Time Calculations for the Crust Layer of the Feed Pile	60
11.0	Residence Time Calculations for the Crust Layer and Glass Pool in Series	63
12.0	Conclusions	68
13.0	Nomenclature	70
14.0	References	74

Figures

3.1: Orientation of Thin Section Obtained from Crucible Sample	5
4.1: Arbitrary Volume Element in the Glass Pool of the SFCM	11
5.1: Origin of Cartesian Coordinate System	16
5.2: Discontinuity in the Mass Fraction $x_{i,gp}$ at the Upper Surface of the Glass Pool	20
5.3: Positive Step Change Introduced into the Glass Pool	21
6.1: Glass Level in the SFCM	26
6.2: BaO Tracer in the Melter Input Stream	27
6.3: MFHT Level Versus Time for the Entire SF-10 Run	28
6.4: Least Squares Fit to the MFHT Level During Time Interval 1	29
6.5: Least Squares Fit to the MFHT Level During Time Interval 2	30
6.6: Least Squares Fit to the MFHT Level During Time Interval 3	31
6.7: BaO Tracer in the Melter Output Stream Compared to a Single, Well-Mixed Tank Model	36
6.8: Residuals Versus Time for a Single, Well-Mixed Tank Model of the BaO Tracer Data	39
6.9: Residuals Versus WPO of BaO for a Single, Well-Mixed Tank Model of the BaO Tracer Data	40
7.1: BaO Tracer in the Melter Output Stream Compared to a Model of Two, Well-Mixed Tanks in Series	45
7.2: Residuals Versus Time for a Two, Well-Mixed Tanks in Series Model of the BaO Tracer Data	46
7.3: Residuals Versus WPO of BaO for a Two, Well-Mixed Tanks in Series Model of the BaO Tracer Data	47
8.1: SrO Tracer in the Melter Input Stream	50
8.2: SrO Tracer in the Melter Output Stream Compared to a Model of Two, Well-Mixed Tanks in Series	51
8.3: Residuals Versus Time for a Two, Well-Mixed Tanks in Series Model of the SrO Tracer Data	52
8.4: Residuals Versus WPO of SrO for a Two, Well-Mixed Tanks in Series Model of the SrO Tracer Data	53
9.1: BaO Tracer in the Melter Output Stream During the Early Part of the Run	56
9.2: Residuals Versus Time for a Two, Well-Mixed Tanks in Series Model of the BaO Tracer Data During the Early Part of the Run	57
9.3: SrO Tracer in the Melter Output Stream Shortly After Injection	58
9.4: Residuals Versus Time for a Two, Well-Mixed Tanks in Series Model of the SrO Tracer Data Shortly After Injection	59
11.1: Response of the Crust Layer to a Positive Step Change in the i th Feed Component	64
11.2: Response of Both the Crust Layer & the Glass Pool to a Positive Step Change in the i th Feed Component	65

Tables

3.1: The SF-10 Target ATM-10-NR Glass Composition	6
3.2: Candidate Tracer Test Matrix	7
3.3: SF-10 Target Glass Compositions	8
3.4: Viscosity Data for Canister Glass WV-10A	9
6.1: Determination of the Mass of the Glass Pool in the SFCM	25
6.2: Least Squares Equations for the MFHT Level Versus Time	32
6.3: Best Parameter Values Obtained From the SF-10 Run for the BaO Tracer	34
7.1: Data Values for the Two, Well-Mixed Tanks in Series Model of the BaO Tracer	44
8.1: Data Values for the Two, Well-Mixed Tanks in Series Model of the SrO Tracer	49
10.1: Comparison of Different Models of the Crust Layer	62
11.1: Mean Residence Times Calculated Using a TWMTIS Model of the SFCM	67

Acknowledgments

The efforts and cooperation of many people were essential for the successful collection and analysis of the tracer data from the SF-10 run. Special thanks are extended to those in the Vitrification Test, Analytical Chemistry, and Process Development Groups who each contributed their special skills to this effort. Thanks also to Michelle Schweickert in Engineering Document Control who bravely conquered the publication of this report.

1.0 Introduction

The use of a chemical tracer to examine mass transport phenomena in a chemical reactor vessel is a powerful tool. The analysis of tracer data can be helpful in understanding and improving the mixing behavior in a vessel, as well as identifying undesirable or abnormal effects.

In this report data are examined that were obtained from the use of two chemical tracers injected into the Slurry Fed Ceramic Melter (SFCM) during FACTS Run SF-10 at the West Valley Demonstration Project. The run was conducted during the 15 day period of May 3 - 18, 1988 for a total of 360 run hours.

2.0 Criteria for the Selection of a Suitable Tracer

Nuclear waste glasses by nature are complicated glass compositions. This results from the wide spectrum of elements present as unrecovered fission products and additional chemicals used during the fuel recycling process.

A great deal of effort went into the design of the appropriate host glass composition specific for the West Valley wastes. Due to the complexity of the product's composition, the optimization of the requisite characteristics of the material was difficult. For acceptable waste glasses, durability and processability factors were balanced to allow safe fabrication of a glass which meets the mandated standards for durability.

As a primary objective of SF-10, the addition of chemical tracers to the slurry feed was used to provide the means to monitor and analyze the mass transport behavior of molten glass in the melter. Ideally, a chemical constituent absent from the initial melter inventory would be found, and a step change (positive for SF-10) would be introduced during the normal course of feeding. The analysis of the glass discharged from the melter then reflects the flow behavior and residence history of its inventory. Once understood, one key toward forecasting the composition of production glass from slurry feed analysis is provided.

It is apparent that to achieve this aim the chemical tracer must behave neutrally in the molten bath of glass. That is, its addition should not perturb the molten solution, thereby neither enhancing nor diminishing its detection in the discharge stream.

Additionally, the specific addition(s) should not significantly alter the properties of the glass system. While remaining a non-radioactive campaign, the simulation should remain as prototypic as possible to that expected during hot operational service.

From the detection standpoint, several requirements need to be met for a successful candidate tracer. First, it should be an element for which reasonable analytical assay accuracy exists. It should also be spiked at a high enough concentration to permit its precise analytical assay. The accuracy and precision of the tracer analysis directly impacts the accuracy and precision of the interpretation of these analyses as they relate to the mixing and residence time information.

Summarizing, a general set of requirements for suitable tracer additives is listed as follows for melter mixing evaluation:

- the tracer should not impact the phase stability of the parent glass system,
- the tracer should not significantly alter the properties of the glass system,
- the tracer should be abundant enough in the system to allow adequate detection, and
- the tracer should be one for which good analytical assay precision and accuracy exists.

3.0 Initial Testing for the Selection and Evaluation of Suitable Tracers

The SF-10 campaign was centered on processing the ATM-10-NR glass composition. This glass composition is shown in Table 3.1, and represents the nonradioactive analog to the most recent vitrification mass balance corrected for the cerium (IV) decon recycle stream.

Since this composition is capable of dissolving a wide variety of materials, the initial test matrix for tracer selection was limited to simple materials commonly used in commercial glasses: barium, strontium, zinc, copper, tin, and cobalt.

Table 3.2 provides the test matrix used for the initial laboratory scale screening studies in units of Weight Percent Oxide (WPO). The tracers shown in the table were added at the twelve indicated levels to a common base slurry (nominally ATM-10-NR). Each of these twelve, one liter preparations were subdivided into four parts: three 125 mL volumes (to be analyzed as slurries), and one 100 mL volume (to be vitrified in a platinum-gold crucible and analyzed as glass). It should be noted at this point, that as a convention, the tracers and their levels of loading are centered on a normalized weight percent as an oxide. This convention is also consistent with the later discussion on the performance of the full scale equipment.

The three 125 mL units of each tracer slurry were compositionally assayed as slurries, to verify adequate ability to monitor the delivery of the tracer in the input stream to the melter. The 100 mL unit in the platinum-gold crucible was dried at 80°C for about 72 hours, and then melted for 24 hours under cover at 1150°C. These samples were then air-quenched to room temperature, visually examined for any abnormalities, then annealed for thin sectioning and analysis.

The quenched melt that resulted resembled a solid bowl, and was sliced to obtain a vertical cross section of glass from the melt (Figure 3.1). Under microscopic analysis, phases which tended to sink or float with respect to the melt could thus be identified.

A small portion of the remainder of each glass sample was compositionally assayed to assure that the discharge of the tracer from the melter could be suitably measured. The entire series of tests proved successful. That is, all of the candidate tracers (Table 3.2) provided no evidence of phase instabilities at the loading levels tested.

Since BaO and SrO were expected to be relatively more soluble in the glass than the other tracer candidates, the test matrix was extended to examine BaO and SrO at higher levels. This reflects experience in commercial glasses, where moderate concentrations of alkaline earths are easily accommodated by glass systems, while transition metal solubilities can vary depending on the particular metal oxide.

Both in the slurry and vitrified forms, each tracer was shown to have an analytical assay precision on the order of 5 relative percent. No attempt was made to determine the actual assay precision for the tracers at this point. Rather, analyses were performed as one set in triplicate and reviewed for deviations in excess of 5 relative percent of the mean. Additionally, the tracer means observed for the feed analyses were compared to the tracer means observed for the glass analyses, and were found to agree to approximately 5 relative percent.

However, for $\text{Co}(\text{OH})_2$ and SnO_2 additional sample preparation was required for suitable assays, potentially increasing the labor intensity and time required for sufficient monitoring of the tracer. While the use of these tracers remains a viable option for future tests, this constraint should be considered as somewhat of a drawback.

Figure 3.1: Orientation of Thin Section Obtained from Crucible Sample

Table 3.1: The SF-10 Target ATM-10-NR Glass Composition

Assumed <u>Oxide</u>	<u>Wt. %</u>
Al ₂ O ₃	6.68
BaO	0.07
B ₂ O ₃	9.51
CaO	0.47
Ce ₂ O ₃	0.13
Cr ₂ O ₃	0.13
Cs ₂ O	0.08
Fe ₂ O ₃	11.50
K ₂ O	3.41
La ₂ O ₃	0.04
Li ₂ O	2.89
MgO	1.24
MnO	1.01
Na ₂ O	10.59
Nd ₂ O ₃	0.16
NiO	0.24
P ₂ O ₅	2.38
RuO ₂	0.02
SO ₃	0.21
SiO ₂	46.24
SrO	0.02
TiO ₂	0.93
Y ₂ O ₃	0.02
ZrO ₂	<u>2.03</u>
	100.00

Table 3.2: Candidate Tracer Test Matrix

<u>Candidate*</u> <u>Tracer</u>	<u>Glass Target WPO</u>	
Ba(OH) ₂ • 8H ₂ O	0.50	1.00
Sr(OH) ₂	0.50	1.00
ZnO	0.20	0.30
Cu(OH) ₂	0.20	0.30
SnO ₂	0.20	0.30
Co(OH) ₂	0.20	0.30

For the SF-10 run, Ba(OH)₂ • 8H₂O and Sr(OH)₂ were chosen as tracers over ZnO and Cu(OH)₂. These selections were based upon both tracers being found acceptable at higher WPO values than those given in Table 3.2, thus allowing large step changes to be imposed during the SF-10 run. ZnO should also be compatible at higher levels (approaching 0.5 WPO), and therefore, may be considered for use in future runs. Cu(OH)₂ introduces an additional consideration, which is redox stability. The Cu(II)/Cu(I) equilibrium is situated in the region at which the WVDP flow sheet is redox controlled. It may be useful in tracking the kinetics of redox transitions, provided a suitable means exists to monitor the Cu(II)/Cu(I) ratio in glasses containing additional multivalent transition metals.

Following the selection of barium and strontium hydroxides as the SF-10 tracers, the target glass compositions for the run were determined. These compositions are provided in Table 3.3, along with the SFCM glass composition at the start of the SF-10 run.

Note that the starting value for neodymium oxide is not reported. In fact, its concentration at the run onset was nearly zero. As prepared, the SF-10 feed contained a modest portion of Nd₂O₃, potentially providing a third tracer for tracking during SF-10. However, like the cobalt and tin, proper detection of this rare earth requires a separate sample preparation, which was beyond the needs of SF-10.

As a final verification test before SF-10, the target composition identified in column three of Table 3.3, was melted in the WVDP Scale Vitrification System (SVS) for a one week campaign (designated SVS-9). Over a 92 hour period, approximately 96 kg of glass were produced. The two tracers monitored in the exit stream (SrO, BaO) attained 90 percent of their respective WPO values in the feed input stream.

Compositional analyses were performed in triplicate on each slurry feed sample (one every four hours), and on every glass discharge sample (one every seven hours). These analyses again indicated reasonable precision on the tracers monitored, on the order of ± 5 relative percent.

* Chemical form used in slurry.

Table 3.3: SF-10 Target Glass Compositions

	Assumed Oxide	SFCM Initial Inventory (WPO)	After First Step Change (WPO)	After Second Step Change (WPO)
(Tracer)	Al ₂ O ₃	7.79	6.65	6.62
	BaO	0.04	0.50	0.50
	B ₂ O ₃	10.31	9.47	9.42
	CaO	0.50	0.47	0.47
	Ce ₂ O ₃	0.06	0.13	0.13
	Cr ₂ O ₃	0.25	0.13	0.13
	Cs ₂ O	0.07	0.08	0.08
	Fe ₂ O ₃	11.34	11.45	11.40
	K ₂ O	3.28	3.40	3.38
	La ₂ O ₃	0.04	0.04	0.04
	Li ₂ O	2.64	2.88	2.87
	MgO	1.18	1.23	1.22
	MnO	1.02	1.01	1.01
	Na ₂ O	10.32	10.54	10.49
	Nd ₂ O ₃	N.R.	0.16	0.16
	NiO	0.38	0.24	0.24
	P ₂ O ₅	2.37	2.37	2.36
	RuO ₂	0.02	0.02	0.02
	SO ₃	0.22	0.21	0.21
	SiO ₂	44.76	46.01	45.79
(Tracer)	SrO	0.05	0.05	0.50
	TiO ₂	0.82	0.93	0.93
	Y ₂ O ₃	0.02	0.02	0.02
	ZrO ₂	<u>2.52</u>	<u>2.02</u>	<u>2.01</u>
		100.00	100.00	100.00

N.R. - Not Reported

WPO - Weight percent as oxide

Following the SVS-9 campaign, each of 13 airlift samples were thin sectioned and compared microscopically for any apparent changes in discharge crystallization as a function of run time. No anomalies or differences were observed.

As a result of these tests, no difficulties were foreseen in the utilization of barium and strontium oxides as tracers for the SF-10 run.

Finally, viscosity data are provided in Table 3.4 for glass extracted from one of the canisters filled during the SF-10 Run. These data will be useful for reference in the event that significantly different compositions are tested in future FACTS or Cold Operational campaigns.

Table 3.4: Viscosity Data for Canister Glass WV-10A

7-11-88-1345-1400-1420

(See Target Table 3.3 "second step")

<u>Temp. (°C)</u>	<u>Log η</u>
1142	1.85
1113	1.95
1084	2.08
1055	2.19
1027	2.28
1000	2.42
969	2.57

where,

$$\log \eta = A + BT + CT^2$$

$$A = 10.8025$$

$$B = -0.122212 \times 10^{-1}$$

$$C = 0.383878 \times 10^{-5}$$

$$T = \text{temperature (°C)}$$

$$\eta = \text{viscosity (poises)}$$

* Data courtesy of the NYS College of Ceramics at Alfred University.

4.0 Development of the General Conservation of Mass Equation

In this section a general equation for the mixing behavior of each of a total of I components in the glass pool of the SFCM will be developed. The basis for the following development is the law of conservation of mass, first applied rigorously to an arbitrary volume element in the glass pool, and then subsequently integrated over the total volume of the glass pool so that a differential equation is obtained which applies to the entire volume of the glass pool in the SFCM.

Referring to Figure 4.1, one can write the following mass balance for the i th component in the slurry feed passing through an arbitrary volume element in the glass pool:

Mass at time $t + \Delta t$

= Mass at time t

+ Mass which enters the front face in the interval Δt

- Mass which leaves the back face in the interval Δt

+ Mass which enters the left face in the interval Δt

- Mass which leaves the right face in the interval Δt

+ Mass which enters the top face in the interval Δt

- Mass which leaves the bottom face in the interval Δt .

(4-1)

Mass transport and chemical reactions in the feed pile floating on the upper surface of the glass pool are considered elsewhere^{1,3}.

Figure 4.1: Arbitrary Volume Element in the Glass Pool of the SFCM

Assuming that the glass density ρ_g is essentially constant at any point (x, y, z) and any time t in the glass pool enables one to write (4-1) mathematically as

$$\begin{aligned}
 & x_{i,gp}(x, y, z, t + \Delta t) \rho_g \Delta x \Delta y \Delta z \\
 = & x_{i,gp}(x, y, z, t) \rho_g \Delta x \Delta y \Delta z \\
 + & x_{i,gp}(x, y, z, t) \rho_g \Delta y \Delta z v_x(x, y, z, t) \Delta t \\
 - & x_{i,gp}(x + \Delta x, y, z, t) \rho_g \Delta y \Delta z v_x(x + \Delta x, y, z, t) \Delta t \\
 + & x_{i,gp}(x, y, z, t) \rho_g \Delta x \Delta z v_y(x, y, z, t) \Delta t \\
 - & x_{i,gp}(x, y + \Delta y, z, t) \rho_g \Delta x \Delta z v_y(x, y + \Delta y, z, t) \Delta t \\
 + & x_{i,gp}(x, y, z, t) \rho_g \Delta x \Delta y v_z(x, y, z, t) \Delta t \\
 - & x_{i,gp}(x, y, z + \Delta z, t) \rho_g \Delta x \Delta y v_z(x, y, z + \Delta z, t) \Delta t \quad \bullet
 \end{aligned} \tag{4-2}$$

Dividing (4-2) through by $\Delta x \Delta y \Delta z \Delta t$ and rearranging gives

$$\begin{aligned}
 & \rho_g \left[x_{i,gp}(x, y, z, t + \Delta t) - x_{i,gp}(x, y, z, t) \right] / \Delta t \\
 = & \rho_g \left[x_{i,gp}(x, y, z, t) v_x(x, y, z, t) \right. \\
 & \left. - x_{i,gp}(x + \Delta x, y, z, t) v_x(x + \Delta x, y, z, t) \right] / \Delta x \\
 + & \rho_g \left[x_{i,gp}(x, y, z, t) v_y(x, y, z, t) \right. \\
 & \left. - x_{i,gp}(x, y + \Delta y, z, t) v_y(x, y + \Delta y, z, t) \right] / \Delta y \\
 + & \rho_g \left[x_{i,gp}(x, y, z, t) v_z(x, y, z, t) \right. \\
 & \left. - x_{i,gp}(x, y, z + \Delta z, t) v_z(x, y, z + \Delta z, t) \right] / \Delta z \quad \bullet
 \end{aligned} \tag{4-3}$$

Now taking $\lim_{\Delta t \rightarrow 0}$, $\lim_{\Delta x \rightarrow 0}$, $\lim_{\Delta y \rightarrow 0}$, and $\lim_{\Delta z \rightarrow 0}$ in (4-3) gives

$$\rho_g \frac{\partial x_{i,gp}}{\partial t} = -\rho_g \frac{\partial (x_{i,gp} v_x)}{\partial x} - \rho_g \frac{\partial (x_{i,gp} v_y)}{\partial y} - \rho_g \frac{\partial (x_{i,gp} v_z)}{\partial z} \quad (4-4)$$

$i = 1, 2, 3, \dots I \quad \bullet$

Equation (4-4) is a general, partial differential equation expressing conservation of mass for each of the I components in the glass pool at any spatial point (x, y, z) and at any time t .

To make (4-4) applicable over the entire volume of the glass pool, let a differential volume dV of the glass pool be defined as

$$dV = dx dy dz \quad (4-5)$$

If (4-4) is multiplied through by dV and integrated over the entire volume of the glass pool one obtains

$$\begin{aligned} \rho_g \iiint \frac{\partial x_{i,gp}}{\partial t} dx dy dz &= -\rho_g \iiint \frac{\partial (x_{i,gp} v_x)}{\partial x} dx dy dz \\ &\quad -\rho_g \iiint \frac{\partial (x_{i,gp} v_y)}{\partial y} dx dy dz \\ &\quad -\rho_g \iiint \frac{\partial (x_{i,gp} v_z)}{\partial z} dx dy dz \\ &\quad \text{for } i = 1, 2, 3, \dots I \quad \bullet \end{aligned} \quad (4-6)$$

Equation (4-6) is the general equation expressing conservation of mass for each of the I components over the entire volume of the glass pool at any time t .

In the following section, the solution to (4-6) will be obtained based upon certain simplifying assumptions. This solution will then be compared to tracer data taken during the SF-10 run in Sections 6.0 through 9.0.

5.0 Solution of the Conservation of Mass Equation for a Well-Mixed Tank

One of the most sweeping assumptions that can be made regarding the conservation of mass equation (4-6) is to assume that the volume of the glass pool is well-mixed. This is generally a good assumption for a vessel in which there is a mechanical agitator present, but is not necessarily true for a glass melter, especially under a wide range of operating conditions. Mixing in the SFCM is due entirely to natural convective flow caused by a relative concentration of electrical power density in certain regions of the glass pool. This concentration generally occurs near the firing surface of each electrode but can be made to occur elsewhere in the glass pool by the manner in which the melter is designed and operated. A relatively high electrical power density in a given region of the glass pool manifests itself by causing a somewhat higher glass temperature there according to Joule's Law (resistance heating). This in turn causes a slight volumetric expansion of the glass which sets up slow circulation (usually with glass velocities on the order of tens of inches/hour) in the glass pool by natural convection. Anything that changes either the power density distribution in the glass pool (for example, resistivity of a glass batch, air-cooling of the electrodes) or the glass viscosity (via batch composition) will affect the natural convective patterns in the glass pool and thus glass mixing.

With the above caveats in mind, one can hypothesize that the SFCM is a well-mixed tank, solve (4-6) for such a condition, and then compare the resulting solution with actual tracer data taken during the SF-10 run.

By definition, if the glass pool is well-mixed, then the mass fraction $x_{i,gp}$ of the i th component is not a function of the spatial coordinates x , y , or z since such dependence would mean that the mass fraction $x_{i,gp}$ is different between two or more points in the glass pool. Mathematically this requirement can be written as

$$x_{i,gp}(x, y, z, t) = x_{i,gp}(t) \quad \text{for } i = 1, 2, \dots, I \quad (5-1)$$

that is, the mass fraction $x_{i,gp}$ is only a function of time. The constraint that (5-1) must hold for each of the I components in the glass pool should be recognized for what it is -- a very strong constraint given that there are a large number of components in the glass pool and no mechanical agitation is present. Scrupulous control of batch composition and melter operating conditions must be maintained if (5-1) is expected to hold. The recent experience at the PAMELA project with ruthenium buildup on the melter floor and the subsequent forced shut down of the melter is a pertinent reminder of what can happen if (5-1) is not true for all glass components.

From (5-1) it follows that if $x_{i,gp}$ is independent of x , y , and z then

$$\frac{\partial x_{i,gp}}{\partial x} = \frac{\partial x_{i,gp}}{\partial y} = \frac{\partial x_{i,gp}}{\partial z} = 0 \quad \bullet \quad (5-2)$$

This means that there can be no gradient of the mass fraction $x_{i,gp}$ in any of the three spatial coordinates if the glass pool is well-mixed.

Using (5-2) in (4-6) gives

$$\begin{aligned}\frac{\partial (x_{i,gp} v_x)}{\partial x} &= x_{i,gp} \frac{\partial v_x}{\partial x} + v_x \frac{\partial x_{i,gp}}{\partial x} \rightarrow 0 \\ &= x_{i,gp} \frac{\partial v_x}{\partial x}\end{aligned}\quad (5-3)$$

and similarly

$$\frac{\partial (x_{i,gp} v_y)}{\partial y} = x_{i,gp} \frac{\partial v_y}{\partial y} \quad (5-4)$$

$$\frac{\partial (x_{i,gp} v_z)}{\partial z} = x_{i,gp} \frac{\partial v_z}{\partial z} \quad (5-5)$$

Now let each term in (4-6) be evaluated separately. Since $x_{i,gp}$ is independent of x , y , and z , the term on the left hand side of (4-6) can be written as

$$\begin{aligned}\rho_g \iiint \frac{\partial x_{i,gp}}{\partial t} dx dy dz &= \rho_g \frac{\partial x_{i,gp}}{\partial t} \iiint dx dy dz \\ &= \frac{\partial x_{i,gp}}{\partial t} M_{gp}\end{aligned}\quad (5-6)$$

where the mass M_{gp} of the glass pool is simply

$$M_{gp} = \rho_g \iiint dx dy dz \quad (5-7)$$

Now suppose that the Cartesian coordinate system shown in Figure 4.1 has its origin at the center of the bottom surface of the feed pile as shown in Figure 5.1. Let the boundaries of the glass pool in the y -direction be denoted by $\pm y^*(z)$, and let the boundaries in the x -direction be denoted by $\pm x^*(z)$. Let the bottom of the feed pile be denoted by $z = 0$, and let the bottom of the glass pool (top of the bottom electrode) be denoted by $z = z^*$.

The first integral on the right hand side of (4-6) can be written as

$$\begin{aligned}-\rho_g \iiint \frac{\partial (x_{i,gp} v_x)}{\partial x} dx dy dz &= -\rho_g \int \int [x_{i,gp} v_x]_{-x^*}^{+x^*} dy dz \\ &= -\rho_g x_{i,gp} \int \int v_x (+x^*, y, {}^{(A)} z, t) dy dz \\ &\quad + \rho_g x_{i,gp} \int \int v_x (-x^*, y, {}^{(B)} z, t) dy dz \quad \bullet\end{aligned}\quad (5-8)$$

Figure 5.1: Origin of Cartesian Coordinate System

The integral marked "A" in (5-8) is the mass flow rate of the *i*th component at the south sidewall of the glass pool. Since the melter throat is located on this sidewall and there may be refractory corrosion on this wall as well, define

$$S_{cor, i, +x^*} = x_{i, gp} W_{pour} = -\rho_g x_{i, gp} \iint v_x(+x^*, y, z, t) dy dz \quad (5-9)$$

Since only corrosion can occur on the north wall of the glass pool at $x = -x^*(z)$, the integral marked "B" in (5-8) can be defined as

$$S_{cor, i, -x^*} = \rho_g x_{i, gp} \iint v_x(-x^*, y, z, t) dy dz \quad (5-10)$$

If there is no corrosion, then the glass velocity v_x at $\pm x^*(z)$ will be zero everywhere except at the glass throat, and the corrosion terms in (5-9) and (5-10) will vanish.

To evaluate the second integral on the right hand side of (4-6), one observes that if the mass fraction $x_{i, gp}$ and the glass velocity v_y are continuous functions, then the order of integration is interchangeable and one can write

$$\begin{aligned} -\rho_g \iiint \frac{\partial (x_{i, gp} v_y)}{\partial y} dx dy dz &= -\rho_g \iiint \left[\frac{\partial (x_{i, gp} v_y)}{\partial y} dy \right] dx dz \\ &= -\rho_g \iint [x_{i, gp} v_y]_{-y^*}^{+y^*} dx dz \\ &= S_{cor, i, +y^*} + S_{cor, i, -y^*} \quad (5-11) \end{aligned}$$

Note that (5-11) is analogous to (5-8) and represents the mass flow rate of the *i*th component on the east ($-y^*(z)$) and west ($+y^*(z)$) sidewalls of the glass pool due to corrosion of the electrodes and refractory.

For simplicity, let the corrosion terms in (5-9), (5-10), and (5-11) be combined into a single term representing corrosion on all four sidewalls of the glass pool and electrodes by defining the total mass flow rate $S_{cor, i}$ of the *i*th component into the glass pool due to corrosion of the refractory and electrodes as

$$\boxed{\begin{aligned} S_{cor, i} &= S_{cor, i, +x^*} + S_{cor, i, -x^*} \\ &+ S_{cor, i, +y^*} + S_{cor, i, -y^*} \quad (5-12) \end{aligned}}$$

It should be noted that for many components in the glass pool (5-12) will be zero simply because such components are not physically present in the melter sidewall and electrode materials of construction.

The third term on the right hand side of (4-6), can be evaluated by interchanging the order of integration to obtain

$$\begin{aligned}
 -\rho_g \iiint \frac{\partial (x_{i,gp} v_z)}{\partial z} dx dy dz &= -\rho_g \iiint \left[\frac{\partial (x_{i,gp} v_z)}{\partial z} dz \right] dx dy \\
 &= -\rho_g \iint [x_{i,gp} v_z]_o^{z^*} dx dy \\
 &= -\rho_g x_{i,gp} \iint v_z(x, {}^{(A)}y, z^*, t) dx dy \\
 &\quad + \rho_g x_{i,gp} \iint v_z(x, {}^{(B)}y, o, t) dx dy \cdot
 \end{aligned} \tag{5-13}$$

The integral marked "A" in (5-13) is the mass flow rate $S_{dep,i}$ of the i th component out of the glass pool by deposition onto the melter floor (bottom electrode). Thus one can define

$$S_{dep,i} = \rho_g x_{i,gp} \iint v_z(x, y, z^*, t) dx dy \cdot \tag{5-14}$$

The integral marked "B" in (5-13) is simply the mass flow rate of the i th component into the glass pool from the bottom of the feed pile at $z = 0$ (Figure 5.1). Since there may be some volatilization of the i th component at the upper surface of the glass pool that is not covered by the feed pile, let the integral "B" be defined as

$$x_{i,co}(t) W_{co} - S_{og,i} = \rho_g x_{i,gp}(t) \iint v_z(x, y, o, t) dx dy \cdot \tag{5-15}$$

When the slurry feed to the melter is off, the mass fraction $x_{i,gp}(t)$ will be constant with depth z (Figure 5.2) if the well-mixed tank assumption given by (5-1) through (5-5) holds. However, when slurry feed is entering the melter and the mass fraction of the i th component emerging from the bottom of the crust layer (on a dried oxide basis) has some value $x_{i,co}(t)$, then $x_{i,gp}$ will generally be discontinuous at $z = 0$ as shown in Figure 5.2.

Having evaluated each of the integral terms in (4-6) individually, one can now use (5-6), (5-9), (5-10), (5-11), (5-12), (5-14), and (5-15) to write (4-6) as a simple differential equation

$$\begin{aligned}
 M_{gp} \frac{d x_{i,gp}}{dt} &= S_{cor,i} - x_{i,GP} w_{POUR} - S_{dep,i} \\
 &\quad + x_{i,co} W_{co} - S_{og,i} \quad i = 1, 2, \dots, I \cdot
 \end{aligned}$$

(5-16)

Equation (5-16) is the conservation of mass equation for each of the I components which enter the glass pool from the feed pile. It is based upon three assumptions:

1. The glass density is constant (or nearly so) over the entire volume of the glass pool.
2. The glass pool is well-mixed.
3. Chemical reaction effects on mass transport in the glass pool are negligibly small.

Equation (5-16) can be solved numerically for a wide range of operating conditions once it has first been shown that the above assumptions are actually valid for the SFCM.

Now if a positive step change in $x_{i,gp}(t)$ is introduced into the glass pool as shown in Figure 5.3, and all other parameters in (5-16) are held constant*, then the following analytical solution to (5-16) can be obtained by conventional techniques,

$$\begin{aligned}
 x_{i,gp}(t) = & x_{i,gp}(0)e^{-W_{pour}t/M_{gp}} \\
 & + \frac{1}{W_{pour}} [x_{i,co}(\infty) W_{co} + S_{cor,i} - S_{dep,i} - S_{og,i}] \times \\
 & [1 - e^{-W_{pour}t/M_{gp}}] \quad .
 \end{aligned}
 \tag{5-17}$$

Since all the parameters (W_{pour} , M_{gp} , $x_{i,co}(\infty)$, etc.) in (5-17) must be held constant in order for this solution to be valid, it is apparent that the time dependent response (or mixing behavior) of $x_{i,gp}(t)$ is strongly dependent upon the mass M_{gp} of the glass pool and the glass pour rate W_{pour} . However, if the glass pour rate is constant, then likewise the glass melt rate W_{∞} must also be constant in order to maintain a constant value of M_{gp} . Therefore one can conclude that the time dependent response of $x_{i,gp}(t)$ is **exponentially dependent** upon the glass melt rate W_{∞} . The glass melt rate is in turn inescapably tied to the mass and energy balances for the feed pile. This dependence of the transport of the i th component through the glass pool upon the glass melt rate cannot be overemphasized.

* This can only be achieved in an approximate sense as will be shown later.

Figure 5.2: Discontinuity in the Mass Fraction $X_{i,gp}$ at the Upper Surface of the Glass Pool

Figure 5.3: Positive Step Change Introduced into the Glass Pool

6.0 Comparison of the BaO Tracer Data to a Single, Well-Mixed Tank Model

One of the objectives of the SF-10 run was to inject suitable tracers into the glass pool of the SFCM and determine its mixing behavior. If the glass pool behaves as a well-mixed tank, then the simple differential equation given by (5-16) and its solution as given by (5-17) should be adequate to describe the response of the glass pool to a positive step change in the mass fraction of the tracer. If not, then it will be necessary to use the more complex, multi-dimensional, conservation of mass equation given by (4-4) or (4-6) to describe the mixing behavior of the SFCM.

Equation (5-17) requires that all quantities except the mass fraction $x_{i,gp}(t)$ and time t be held constant in order for it to be a valid solution of (5-16). More specifically, (5-17) sets the following experimental criteria:

Criterion #1:

The glass pour rate W_{pour} must be held constant. This is not practical in the SFCM since glass is poured in batches using an airlift technique. However, if one averages the amount of glass removed from the melter over a long period of time, then an average glass pour rate can be determined which will approximately satisfy this requirement.

Criterion #2:

The mass of the glass pool M_g must be held constant. If one assumes a constant value for the glass density ρ_g , then this requirement really means that the volume of the glass pool must be held constant. Again, the airlift technique for pouring glass from the SFCM prevents this requirement from being rigorously enforced, but it can be approximately satisfied by using the average glass pool volume computed over a long period of time.

Criterion #3:

The mass fraction $x_{i,sl}(\infty)$ of the tracer in the input stream to the SFCM must be held constant so that the mass fraction $x_{i,\infty}(\infty)$ emerging from the bottom of the crust layer will be constant. This was achieved by placing the tracer in the Melter Feed Hold Tank (MFHT) from which slurry feed was directly fed to the melter. This tank is equipped with a mechanical agitator which served to homogenize the tracer in the MFHT. Note that the MFHT agitator must remain on in order to hold $x_{i,sl}(\infty)$ at a constant value.

Criterion #4:

The glass melt rate W_∞ must be held constant. Since there is no way to directly control the plenum temperature in the SFCM, and thermal radiation from the plenum is a significant (and sometimes dominant) energy source that affects glass melting ^{4,6}, the only way to satisfy this requirement is to select a glass melt rate that the SFCM can be reasonably expected to maintain when the plenum refractory cools down from an initially high temperature (900 to 1000°C) at the start of the melter run to its steady-state value (300 to 500°C). A slurry feed rate target of 80 liters/hr was selected for the SF-10 run and held as constant as practical throughout the run. This in turn provided a constant target glass melt rate of 29.0 kg/hr.

Criterion #5:

The corrosion rate $S_{\text{cor},i}$ of the tracer entering the glass pool due to corrosion of the electrodes and refractory must be constant. This was satisfied by selecting two tracers (BaO and SrO) which are not present in either the refractory or electrode materials. Thus this term was easily held at a constant value of zero.

Criterion #6:

The deposition rate $S_{\text{dep},i}$ and the volatilization rate $S_{\text{og},i}$ must be held constant. No attempt was made to control these terms in the SF-10 run since their magnitude was thought to be negligibly small for the tracers that were used.

With the above experimental criteria in mind, the tracer portion of the SF-10 run was begun on May 3, 1988 and continued through May 15, 1988 for a total of 360 run hours. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ was added to the MFHT as a water-soluble tracer before the start of the run to provide a positive step change in BaO^* to the SFCM at time $t = 0$. Since the run started from an idling condition in the SFCM, there was no feed pile present initially and the melter plenum was very hot (roughly 900°C). The feed pile formed very quickly when slurry feed to the melter began, but grew in diameter as the run progressed and the plenum temperature cooled down to a steady-state value of 451°C .

To determine the effect of the feed pile on the mixing behavior in the SFCM, a second tracer, $\text{Sr}(\text{OH})_2^*$, was added to the MFHT at time $t = 123$ hours. At this point both the plenum temperature and the feed pile had reached steady-state. The objective was to compare the results of both tracers to see if the effects of the feed pile could be detected.

At the start of the run, both the slurry feed stream and the melter output stream were sampled at one hour intervals until 12 run hours had elapsed. The sampling frequency for each stream was then changed to every 4 hours.

At time $t = 123$ run hours when the $\text{Sr}(\text{OH})_2$ was added to the MFHT, the feed stream and melter output stream sampling frequencies were changed back to once an hour for the next 12 run hours. The sampling frequency was then dropped back to every 4 hours. Throughout the run, multiple analyses and occasionally multiple samples, were taken to assist in the statistical determination of the precision in the chemical analyses.

Before attempting to apply (5-17) to the tracer data obtained from the run, it is necessary to determine if the above six experimental criteria were actually satisfied.

The total amount of glass poured during the run was roughly 9,525 kg. Total run time was 360 hours. This gives an average glass pour rate W_∞ of 26.46 kg/hr, satisfying Criterion #1.

$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ decomposes in the melter according to the reaction:
 $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O} \rightarrow \text{BaO} + 9\text{H}_2\text{O}\uparrow$

The data in both the melter input and output streams are reported in units of weight percent oxide (WPO) of BaO. Therefore, the tracer will hereafter be referred to as BaO.

$\text{Sr}(\text{OH})_2$ decomposes in a manner similar to $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. It is also reported in units of WPO and will hereafter be referred to as SrO.

The mass M_{gp} of glass in the glass pool averaged over the run was determined as shown in Table 6.1. The design volume of the glass pool at room temperature was taken as 860 liters*. Volumetric expansion of the refractory up to operating temperature was estimated to increase the design volume by 21 liters. The effect of pouring and refilling of the glass pool with newly melted glass after each airlift was estimated using Figure 6.1 which gives a mean glass level in the pool of 26.35 inches. Assuming that the glass started to ooze over the discharge trough at the upper data points in Figure 6.1 (approximately 26.9 inches), the volume reduction due to glass pouring and refilling was calculated to be 31 liters based upon a $2.2m^2$ upper surface area of the glass pool. The volume of glass displaced by the feed pile was calculated using an existing model of the feed pile reported previously^{4,6}, and found to be approximately 106 liters. The average mass of the glass in the glass pool was then determined to be approximately 1786 kg and was used as the value of M_{gp} in (5-17) to satisfy Criterion #2.

Figure 6.2 shows the Weight Percent Oxide (WPO) of BaO in the slurry feed stream to the melter. These data were measured by the Induction Coupled Plasma (ICP) technique and are reported as weight percent oxide rather than mass fraction $x_{i,sl}(t)$. However, the two are directly proportional and may be used interchangeably in the equations developed in Sections 4.0 and 5.0 for the glass pool as long as they are not mixed. Reporting the tracer data for the slurry feed stream in units of WPO has the additional advantage that the effects of water in the slurry and gaseous decomposition in the feed pile are removed from the data. This permits direct comparison of WPO values in the slurry feed stream with WPO values in the melter output stream.

Note that Figure 6.2 shows that the BaO tracer provided a step change from 0 to 0.4570 WPO of BaO in the melter input stream (slurry feed) at time $t = 0$. The standard deviation of these data (σ in Figure 6.2) was calculated to be 0.0247 (5.40 percent of the mean) for the duration of the run. Thus the weight percent oxide of BaO in the melter input stream $WPO_{i,sl}(\infty)^{**}$ was determined to be 0.4570. This satisfies Criterion #3.

The glass melt rate W_{∞} was held constant by holding the volumetric slurry feed rate W_s^* constant as measured by the falling slurry level L_{sl} in the MFHT. The slurry level L_{sl} is related to the volumetric slurry feed rate W_s^* by the following mass balance

$$\rho_{sl} A_t \frac{d L_{sl}}{dt} = -\rho_{sl} W_{sl}^* \quad (6-1)$$

which can be integrated over time t to give the slurry level in the MFHT at any time t as

$$L_{sl}(t) = \frac{-W_{sl}^* t}{A_t} + L_{sl}(0) \quad (6-2)$$

if the slurry feed rate W_s^* is constant.

* Personal communication with L. L. Petkus.

** Note that since the slurry sample was dried and then converted to an oxide during the ICP analysis, then $WPO_{i,sl}(\infty) = WPO_{i,ox}(\infty)$ •

Figure 6.3 shows the slurry level in the MFHT for the entire run. The two sharp upward spikes at 120 and 220 run hours correspond to additions of slurry to the MFHT from another tank.

If Figure 6.3 is divided into three time intervals and each interval is fitted with a least squares straight line as required by (6-2), then the equation for each time interval is as given in Figures 6.4 through 6.6.

Table 6.1: Determination of the Mass of the Glass Pool in the SFCM

Design volume at room temperature	860 liters
Correction for thermal expansion	+ 21 liters
Correction for pouring and refilling after each airlift	-31 liters
Correction for glass displaced by the feed pile	<u>-106 liters</u>
Final corrected volume	744 liters
Mass of glass pool at a glass density of 2.40 kg/l	1786 kg

Figure 6.1: Glass Level in the SFCM

Figure 6.2: BaO Tracer in the Melter Input Stream

Figure 6.3: MFHT Level Versus Time for the Entire SF-10 Run

Figure 6.4: Least Squares Fit to the MFHT Level During Time Interval 1

Figure 6.5: Least Squares Fit to the MFHT Level During Time Interval 2

Figure 6.6: Least Squares Fit to the MFHT Level During Time Interval 3

Table 6.2: Least Squares Equations for the MFHT Level Versus Time

Interval	Time	Figure	$L_{sl}^*(t)$ Equation	σ
1	0-120 hrs	6.4	$-0.5747t + 131.6$	1.519
2	120-219 hrs	6.5	$-0.5971t + 174.7$	1.396
3	219-360 hrs	6.6	$-0.5914t + 232.9$	1.481

If there are J_1 data points in the first time interval of Table 6.2, then the residual e_j can be defined⁷ as the difference between the measured level $L_{sl,j}$ and the predicted level $L_{sl,j}^*$ calculated by the least squares regression, that is,

$$e_j = L_{sl,j} - L_{sl,j}^* \quad , \quad \text{for } j = 1, 2, \dots, J_1 \quad (6-3)$$

The standard error of regression σ_e is defined in this case as⁷

$$\sigma_e = \left[\frac{\sum_{j=1}^{J_1} e_j^2}{J_1 - 2} \right]^{1/2} \quad (6-4)$$

and is a measure of the error between the measured data points and the least squares fit.* For example, at time $t = 0$ in Figure 6.4, σ_e is 1.15 percent of the MFHT level, and at time $t = 120$ hours, σ_e is 2.43 percent of the MFHT level. This simply means that the least squares fit approximates the data very well and that (6-2) has the correct functional form.

However, the primary concern is maintaining a constant slurry feed rate W_{sl}^* . If (6-2) is differentiated with respect to time t , then one obtains

$$\frac{d L_{sl}}{dt} = \frac{-W_{sl}^*}{A_t} \quad (6-5)$$

or

$$W_{sl}^* = -A_t \frac{d L_{sl}}{dt} \quad (6-6)$$

and it is apparent that the slurry feed rate W_{sl}^* is directly proportional to the slope of L_{sl} .

* Note that σ_e is equivalent to the standard deviation about a mean value.

In this case $L_{sl,j}^*$ is comparable to the usual definition of the mean.

To estimate the error in the slurry feed rate, let the integral average of the slope in tank level L_{sl} be calculated from Table 6.2 as

$$\begin{aligned}\frac{d L_{sl}}{dt} &= \frac{\int_0^{360} \left[\frac{d L_{sl}}{dt} \right] dt}{\int_0^{360} dt} \\ &= [-0.5747 (120) - 0.5971 (219-120) - 0.5914 (360-219)] / 360 \\ &= -0.5874 \text{ inches/hr} \quad \bullet\end{aligned}\tag{6-7}$$

In a manner analogous to (6-3) and (6-4), let the error of regression for the slope of L_{sl} be approximated as

$$\begin{aligned}\sigma_e(\text{slope}) &= \left[\frac{\int_0^{360} \left[\frac{d L_{sl}}{dt} - \frac{d L_{sl}}{dt} \right]^2 dt}{\int_0^{360} dt} \right]^{1/2} \\ &= \{ [(-0.5747 + 0.5874)^2 (120) \\ &\quad + (-0.5971 + 0.5874)^2 (219-120) \\ &\quad + (-0.5914 + 0.5874)^2 (360-219)] / 360 \}^{1/2} \\ &= 0.009360 \text{ inches/hr} \quad \bullet\end{aligned}\tag{6-8}$$

Using (6-7) and (6-8) in (6-6) gives

$$W_{sl}^* = -A_t \left[\frac{d L_{sl}}{dt} \pm \sigma_e(\text{slope}) \right], \tag{6-9}$$

or an average slurry feed rate for the entire run of

$$W_{sl}^* = 76.7 \frac{\text{liters}}{\text{hr}} \pm 1.22 \quad \bullet\tag{6-10}$$

This assumes zero error in the tank area A_t and zero error in the calibration of the level transmitter LT-1101. These errors are of course, not precisely zero but will be examined elsewhere*. The point here is to show that the slurry feed rate **averaged over the entire run** was held constant with excellent precision [small $\sigma_e(\text{slope})$] although there were occasional brief feed interruptions and

* The level in the MFHT has currently been calibrated as a function of LT-1101 but the results have not yet been reported.

upsets. This constant slurry feed rate W_{s1} in turn gives a constant glass melt rate W_{∞} of approximately $29.04 \frac{kg}{hr} \pm 0.462$, which satisfies Criterion #4.

Criterion #5 was automatically satisfied (as mentioned previously by the choice of tracers).

Criterion #6 was assumed to be automatically satisfied due to negligible deposition and off-gas losses.

Thus it can be concluded at this point that the six experimental criteria required for (5-17) to be a valid solution of the conservation of mass equation (5-16) for a well-mixed tank were all satisfied as closely as practical during the SF-10 run. One must now determine if the well-mixed tank hypothesis is indeed an adequate model of mass transport (and thus glass mixing) in the SFCM.

The best values of each parameter to use in (5-17) for analysis of the SF-10 run are summarized in Table 6.3 along with estimates of their error (precision) where available.* The glass pour rate W_{pour} differs from the glass melt rate W_{∞} by roughly 9 percent. These two values must be equal for the constant slurry feed condition maintained throughout the run. The melt rate W_{∞} is thought to be the more accurate of the two.

Table 6.3: Best Parameter Values Obtained From the SF-10 Run for the BaO Tracer

$WPO_{i,GP}(0) = 0.03709 \pm 0.00124$	$W_{\infty} = 29.04 \frac{kg}{hr} \pm 0.462$
$W_{pour} = 26.5 \text{ kg/hr}$	$S_{cor,i} = 0$
$M_{BP} = 1786 \text{ kg}$	$S_{dep,i} = 0$
$WPO_{i,GP}(\infty) = 0.4570 \pm 0.0247$	$S_{og,i} = 0$

Therefore let

$$W_{pour} = W_{\infty} \quad (6-11)$$

in (5-17).

* Estimates of the true "accuracy" of these data (which incorporates instrument calibration errors) is not currently available.

Using the data in Table 6.3 and writing (5-17) in terms of the Weight Percent Oxide ($WPO_{i,RP}$) instead of mass fraction $x_{i,RP}$ gives the following equation for BaO in the output stream from the melter

$$\begin{aligned} WPO_{i,RP}(t) &= WPO_{i,RP}(o) e^{-W_{co}t/M_{gp}} \\ &+ WPO_{i,co}(\infty) [1 - e^{-W_{co}t/M_{gp}}] \\ &= WPO_{i,co}(\infty) \\ &- [WPO_{i,co}(\infty) - WPO_{i,RP}(o)] e^{-W_{co}t/M_{gp}} \end{aligned}$$

or simply

$WPO_{i,RP}(t) = 0.4570 - 0.4200 e^{-0.01626t}$ <p style="text-align: center; margin: 0;">(SWMT model)</p>	(6-12)
--	--------

Figure 6.7 shows the BaO tracer data measured in the melter output stream compared to the Single, Well-Mixed Tank (SWMT) model of the glass pool given by (6-12). Although the effect of the feed pile is not considered in this model, the agreement between the model and the data appears reasonably good.

To obtain a quantitative measure of the goodness of fit between the SWMT model and the data, it is helpful to examine the following statistical measures of the fit.

Let the residual e_{ij} of the i th component at the j th time value in Figure 6.7 be defined in a manner analogous to (6-3), for example,

$$e_{ij} = WPO_{i,RPj} - WPO_{i,RPj}^* \quad j = 1, 2, \dots, J_1 \quad (6-13)$$

where $WPO_{i,RPj}$ is the measured value of the weight percent oxide of the i th component at the j th time value, and $WPO_{i,RPj}^*$ is the calculated value from (6-12).

The standard error of regression is defined in this case (zero degrees of freedom) as

$$\sigma_{e,i} = \left[\frac{\sum_{j=1}^{J_1} e_{ij}^2}{J_1} \right]^{1/2} \quad (6-14)$$

and is a measure of the **magnitude** of the error between the measured data points and calculated data points, regardless of the algebraic sign of the residuals e_{ij} .

----	RAW DATA
=====	RAW DATA
-----	SINGLE WELL-MIXED TANK
-----	(FEEDPILE NEGLECTED)

Figure 6.7: BaO Tracer in the Melter Output Stream Compared to a Single, Well-Mixed Tank Model

For example, from (6-13) one can write that the measured value $WPO_{i,gpj}$ of the i th component at the j th time value is simply

$$\begin{aligned} WPO_{i,gpj} &= WPO_{i,gpj}^* + e_{ij} \\ \text{for } j &= 1, 2, \dots, J_1 \end{aligned} \quad (6-15)$$

that is, the measured value is equal to the calculated value $WPO_{i,gpj}^*$ plus some residual error e_{ij} .

To predict the measured value $WPO_{i,gp}(t)$ at some arbitrary time t , one would expect that this new value is given by

$$WPO_{i,gp}(t) = WPO_{i,gp}^*(t) + e_i(t) \quad (6-16)$$

where $e_i(t)$ is the residual at time t . This residual $e_i(t)$ is approximately given by the standard error of regression $\sigma_{e,i}$. Therefore, the measured value of $WPO_{i,gp}(t)$ can be closely predicted as

$$WPO_{i,gp}(t) \approx WPO_{i,gp}^*(t) \pm \sigma_{e,i} \quad (6-17)$$

The coefficient of determination R^2 is defined as⁷

$$R^2 = 1 - \frac{\sum_j [WPO_{i,gpj} - WPO_{i,gpj}^*]^2}{\sum_j [WPO_{i,gpj} - \overline{WPO}_{i,gp}]^2} \quad (6-18)$$

where the average value $\overline{WPO}_{i,gp}$ is simply

$$\overline{WPO}_{i,gp} = \frac{1}{J_1} \sum_j^{J_1} WPO_{i,gpj} \quad (6-19)$$

The coefficient of determination always falls in the interval

$$0 \leq R^2 \leq 1 \quad (6-20)$$

and can be interpreted as that portion of the variation in WPO versus time t that is explained by the model. For example, in Figure 6.7 the R^2 value is 0.9593, which means that 96 percent of the time dependent behavior of the measured WPO values of BaO is explained by the SWMT model given by (6-12). This is quite good, especially when one reflects upon the choice of a well-mixed tank assumption in a vessel without forced agitation of the contents.

The correlation coefficient R is simply the square root of the coefficient of determination R^2 . Values of R fall in the range

$$-1 \leq R \leq +1 \quad (6-21)$$

and have the following interpretation*:

1. When $R = 0$, there is no correlation between the measured values of $WPO_{i,gp,j}$ and the model values $WPO_{i,gp,j}^*$.
2. When R is near -1 , small measured values of $WPO_{i,gp,j}$ tend to occur with large model values $WPO_{i,gp,j}^*$ and vice versa. This is negative correlation.
3. When R is near $+1$, small measured values of $WPO_{i,gp,j}$ are accompanied by small model values $WPO_{i,gp,j}^*$. Likewise there is good agreement at large values. This is positive correlation and is a major objective of the modeling process.

Returning to Figure 6.7, it can be seen that the standard error of regression $\sigma_{e,j}$ is moderately small, and the values of R and R^2 are both very close to unity. The high value of R indicates good positive correlation, and the value of R^2 indicates that the model explains 96 percent of the time dependent behavior of the measured data.

The validity of the SWMT model can be scrutinized even further by examining the time dependent behavior of the residuals $e_{i,j}$ defined by (6-13) and shown in Figure 6.8. Ideally these residuals should be randomly distributed in a band about zero. However there is an observable trend in these data from negative to positive with increasing time. This suggests that either the residuals are not truly random (they could be caused for example, by process upset conditions that invalidate the positive step change solution to the conservation of mass equation) or that the well-mixed tank model could be improved by the addition of one or more terms to treat other effects occurring in the melter.

Furthermore, since the residuals are all negative during the early part of the run, this means that the model is overpredicting the WPO of BaO during the early part of the run. Some type of effect is apparently delaying the transport of the tracer through the glass pool.

If the residuals $e_{i,j}$ are plotted as a function of the $WPO_{i,gp,j}$ values for BaO as shown in Figure 6.9, an observable trend from negative to positive is again noted. This trend is negative for small values of $WPO_{i,gp,j}$, but positive for large values. However, these residuals should also be randomly distributed about zero with no observable trend. The presence of a trend again suggests that the model could be improved, particularly for small values of $WPO_{i,gp,j}$.

Thus there is a statistical basis for concluding that the SWMT model could be improved upon, especially for small values of time t and small values of $WPO_{i,gp,j}$, that is, the early part of the run.

Since the model neglects the presence of the feed pile in the melter, there is a good physical basis for suspecting that the model might be improved by considering the effect of the feed pile on the tracer behavior. In the following section, the model will be modified to include this effect.

Figure 6.8: Residuals Versus Time for a Single, Well-Mixed Tank Model of the BaO Tracer Data

Figure 6.9: Residuals Versus WPO of BaO for a Single, Well-Mixed Tank Model of the BaO Tracer Data

7.0 Comparison of the BaO Tracer Data to a Two, Well-Mixed Tanks in Series Model

Since the residence time of both liquids and solids in the slurry layer of the feed pile is expected to be negligibly small^{2,3}, it is probably sufficient to model the feed pile as only a single layer -- the crust layer. Furthermore, since Figure 6.7 shows no evidence of plug flow in the measured tracer data, let the crust layer of the feed pile be approximated as the first of two, well-mixed tanks in series. The second tank will, of course, be the glass pool beneath the feed pile. In the following discussion the appropriate equations for this type of model will be developed, and then compared to the BaO tracer data.

The conservation of mass equation for the *i*th component in the crust layer of the feed pile can be written on a dried oxide basis as

$$f_{sg} M_c \frac{d x_{i,c}}{dt} = x_{i,sl} W_{sl}^* \rho_{sl} f_s f_{sg} - x_{i,co} W_{co} \quad (7-1)$$

in terms of the mass fraction $x_{i,c}$ in the crust layer, the mass fraction $x_{i,sl}$ in the slurry layer, and the mass fraction $x_{i,co}$ in the melting glass emerging from the bottom of the crust layer of the feed pile.

The well-mixed tank assumption requires that

$$x_{i,c} = x_{i,co} \quad (7-2)$$

and leads to the solution

$$x_{i,c}(t) = x_{i,c}(0) e^{-W_{co}t/(f_{sg} M_c)} + \frac{x_{i,sl}(t) W_{sl}^* \rho_{sl} f_s f_{sg}}{W_{co}} \left[1 - e^{-W_{co}t/(f_{sg} M_c)} \right] \quad (7-3)$$

Since all of the tracer data are reported on a weight percent oxide basis, the following mass balances are necessary in order to convert (7-3) to a weight percent oxide basis:

$$x_{i,c} = \text{WPO}_{i,c} / 100 \quad (7-4)$$

$$x_{i,sl} = \text{WPO}_{i,sl} / 100 \quad (7-5)$$

Substituting (7-4) and (7-5) in (7-3) gives

$$\begin{aligned}
WPO_{i,co}(t) = & WPO_{i,co}(0)e^{-W_{co}t/(f_{sg} M_c)} \\
& + \frac{WPO_{i,sl}(t) W_{sl}^* \rho_{sl} f_s f_{sg}}{W_{co}} \left[1 - e^{-W_{co}t/(f_{sg} M_c)} \right] \cdot
\end{aligned}
\tag{7-6}$$

(crust layer of feed pile)

For a positive step change in the weight percent oxide of the BaO tracer in the slurry feed one has that

$$\begin{aligned}
WPO_{i,sl}(t) &= 0, \quad t < 0 \\
&= WPO_{i,sl}(\infty), \quad t \geq 0 \quad \bullet
\end{aligned}
\tag{7-7}$$

Equation (7-6) represents the weight percent oxide of the BaO tracer as it leaves the bottom of the crust layer of the feed pile and enters the glass pool. This equation is based upon two assumptions:

1. The slurry layer of the feed pile has a negligible effect on mass transport of the tracer.
2. The crust layer of the feed pile is well-mixed.

The use of (7-6) means that the weight percent oxide of BaO entering the glass pool from the crust layer of the feed pile is now time dependent, and is not the simple, positive step change that was used previously to obtain (5-17) from (5-16). This requires a new solution to (5-16), which can be obtained as follows.

Using a Taylor's series expansion of the mass fraction $x_{i,gp}(t)$, one can write

$$\begin{aligned}
x_{i,gp}(t) = & x_{i,gp}(t - \Delta t) + \frac{\Delta t}{dt} \frac{dx_{i,gp}(t - \Delta t)}{dt} \\
& + \frac{\Delta t^2}{2} \frac{d^2 x_{i,gp}(t - \Delta t)}{dt^2} + \dots
\end{aligned}
\tag{7-8}$$

or

$$\begin{aligned}
\frac{d x_{i,gp}(t - \Delta t)}{dt} &= \frac{x_{i,gp}(t) - x_{i,gp}(t - \Delta t)}{\Delta t} \\
&- \frac{\Delta t}{2} \frac{d^2 x_{i,gp}(t - \Delta t)}{dt^2} - \dots \\
&= \frac{x_{i,gp}(t) - x_{i,gp}(t - \Delta t)}{\Delta t}, \text{ if } \Delta t \text{ small.}
\end{aligned}
\tag{7-9}$$

Using (7-9) in (5-16) gives

$$\begin{aligned}
M_{gp} \left[\frac{x_{i,gp}(t) - x_{i,gp}(t - \Delta t)}{\Delta t} \right] \cong & - S_{cor,i} - x_{i,gp}(t) W_{pour} \\
& - S_{dep,i} + x_{i,co}(t) W_{co} \\
& - S_{og,i}
\end{aligned} \tag{7-10}$$

which can be solved for the mass fraction $x_{i,gp}(t)$ to obtain

$$\begin{aligned}
x_{i,gp}(t) \cong & - \left[S_{cor,i} - S_{dep,i} + x_{i,co}(t) W_{co} - S_{og,i} \right. \\
& \left. + \frac{M_{gp} x_{i,gp}(t - \Delta t)}{\Delta t} \right] / \left[\frac{M_{gp}}{\Delta t} + W_{pour} \right], \text{ for } \Delta t \text{ small.}
\end{aligned} \tag{7-11}$$

Alternatively, (7-11) can be expressed in terms of weight percent oxide by noting that

$$x_{i,gp}(t) = WPO_{i,gp}(t)/100 \tag{7-12}$$

$$x_{i,co}(t) = WPO_{i,co}(t)/100 \tag{7-13}$$

to obtain

$$\begin{aligned}
WPO_{i,gp}(t) \cong & - 100 \left[S_{cor,i} - S_{dep,i} + \frac{WPO_{i,co}(t) W_{co}}{100} - S_{og,i} \right. \\
& \left. + \frac{M_{gp} WPO_{i,gp}(t - \Delta t)}{100 \Delta t} \right] / \left[\frac{M_{gp}}{\Delta t} + W_{pour} \right], \\
& \text{for } \Delta t \text{ small. (glasspool)}
\end{aligned} \tag{7-14}$$

Equations (7-6) and (7-14) represent a model of the SFCM consisting of Two, Well-Mixed Tanks in Series (TWMTIS). Values for each term in (7-6) and (7-14) are given in Table 7.1 for use with the BaO tracer data obtained from the SF-10 run. Note that the data for the glass pool are the same as those in Table 6.3.

Table 7.1: Data Values for the Two, Well-Mixed Tanks in Series Model of the BaO Tracer

$f_s = 0.47$	$W_{sl}^* = 76.7 \frac{\text{litres}}{\text{hr}} \pm 1.22$
$f_{sg} = 0.601$	$W_{pour} = 29.04 \frac{\text{kg}}{\text{hr}} \pm 0.462$
$M_c = 351.4 \text{ kg}$	$WPO_{i,co} = 0.03709 \pm 0.00124$
$M_{gp} = 1786 \text{ kg}$	$WPO_{i,gp}(0) = 0.03709 \pm 0.00124$
$S_{cor,i} = 0$	$WPO_{i,sl}(\infty) = 0.4570 \pm 0.0247$
$S_{dep,i} = 0$	$\Delta t = 1 \text{ to } 4 \text{ hours}$
$S_{og,i} = 0$	$\rho_{sl} = 1.34 \text{ kg/liter}$
$W_{co} = 29.04 \frac{\text{kg}}{\text{hr}} \pm 0.462$	

Equations (7-6) and (7-14) were programmed using the RS/1 software package available on site. A variable time step size was used in order to obtain a calculated value from the model for each measured value of BaO to facilitate pointwise statistical analysis of the model.

Figure 7.1 shows the TWMTIS model compared to the measured values of BaO in the output stream of the SFCM. This fit appears somewhat better to the eye than the SWMT model shown in Figure 6.7.

If one compares the statistical measures in Figures 6.7 and 7.1, it is apparent that the TWMTIS model is indeed slightly better than the SWMT model by all accounts. However, the difference between the two models is not large.

Inspecting the TWMTIS model further, one observes that when the residuals e_{ij} are plotted versus time for this model (Figure 7.2), they now appear somewhat more randomly distributed about zero than for the SWMT model (cf. Figure 6.8). This further confirms that the TWMTIS model is somewhat better than the SWMT model.

Figure 7.3 shows the residuals e_{ij} for the TWMTIS model as a function of weight percent oxide of BaO. If this figure is compared to the corresponding figure for the SWMT model (Figure 6.9), it can be seen that the residuals in Figure 7.3 also appear more randomly distributed about zero than those in Figure 6.9. This again indicates that the TWMTIS model is somewhat better than the SWMT model. However, the TWMTIS model is still not perfect, since it fails to produce a completely random distribution of the residuals e_{ij} about zero in Figures 7.2 and 7.3. Some other minor effects must be present in the mixing behavior of the SFCM, but since the TWMTIS model accounts for 97 percent of the time dependent behavior of the BaO tracer ($R^2 = 0.9667$ in Figure 7.1), one can conclude that this model gives a good description of the mixing behavior of the BaO tracer in the SFCM.

Figure 7.1: BaO Tracer in the Melter Output Stream Compared to a Model of Two, Well-Mixed Tanks in Series

Figure 7.2: Residuals Versus Time for a Two, Well-Mixed Tanks in Series Model of the BaO Tracer Data

Figure 7.3: Residuals Versus WPO of BaO for a Two Well-Mixed Tanks in Series Model of the BaO Tracer Data

8.0 Comparison of the SrO Tracer Data to the Two, Well-Mixed Tanks in Series Model

Since there was no feed pile present in the SFCM at the start of the SF-10 run, the BaO tracer initially was injected directly onto the surface of the glass pool as the slurry feed entered the melter. A feed pile quickly formed however, and then slowly increased in both diameter and thickness as the plenum refractory cooled down to its steady-state temperature of 451°C.

In an effort to determine the effect of a growing feed pile and also to examine the mixing behavior of the SFCM after true steady-state operating conditions were achieved, a second tracer, $\text{Sr}(\text{OH})_2^*$, was added to the MFHT at time $t = 123$ hours to produce a second, positive step change in the slurry feed to the melter.

Figure 8.1 shows the $\text{Sr}(\text{OH})_2$ tracer in the slurry feed reported in units of weight percent oxide of SrO. When the run started, there was an initial level of SrO already present in the glass at a mean level of 0.05589 WPO with standard deviation (sigma in Figure 8.1) of 0.00222 WPO. At time $t = 123$ hours, the level of $\text{Sr}(\text{OH})_2$ in the slurry feed was increased to give a level of SrO in the feed of 0.5207 WPO ± 0.0630 . This level was then held constant until the run was terminated at time $t = 360$ hours. At the time this tracer was introduced, the feed pile, plenum, and glass pool were all at steady-state operating conditions. Thus these tracer data should give a good representation of the mixing behavior of the SFCM under continuous, steady-state conditions during radioactive operation.

Figure 8.2 shows the SrO tracer data in the melter output stream.

The initial level of 0.05414 WPO ± 0.00248 of SrO in the melter output stream agrees favorably with that reported in the input stream (Figure 8.1) up until the time that the step change in SrO was introduced. The data for $t \geq 123$ hours are compared to the TWMTIS model (defined by (7-6) and (7-14)), that was used to model the BaO tracer data in Figure 7.1. All of the input data values to the model are the same as those in Table 7.1 with the exception of the terms relating to the initial and final values of SrO in the slurry feed stream. These values were taken from Figures 8.1 and 8.2, and are tabulated in Table 8.1.

* Recall that $\text{Sr}(\text{OH})_2$ decomposes to SrO as noted earlier, and will be referred to hereafter as SrO.

Table 8.1: Data Values for the Two, Well-Mixed Tanks in Series Model of the SrO Tracer

$$WPO_{i,\infty}(o) = 0.05414 \pm 0.00248$$

$$WPO_{i,gp}(o) = 0.05414 \pm 0.00248$$

$$WPO_{i,sl}(\infty) = 0.52070 \pm 0.06300$$

Figure 8.2 shows that the TWMTIS model gives an excellent fit to the SrO data. The standard error of regression $\sigma_{e,i}$ is moderately small, the correlation coefficient R is high, and the coefficient of determination R^2 indicates that the model explains 97 percent of the time dependent behavior of the tracer.

Figures 8.3 and 8.4 show the residuals $e_{i,j}$ calculated for the fit between the TWTIS model and the SrO tracer data when plotted as functions of run time and WPO of SrO. Both figures show a roughly random distribution of the residuals about zero, which further confirms the excellent fit of the model to the data.

If the BaO tracer data (Figures 7.1 through 7.3) are compared with the SrO tracer data (Figures 8.2 through 8.4), it is apparent that the TWMTIS model fits the SrO data slightly better than it fits the BaO data. Since the BaO data were measured with a slowly growing feed pile, and the SrO data were measured with a fully developed feed pile, one might hypothesize that the effect of the growing feed pile in the BaO data has some impact on the mixing behavior of the SFCM. In the following section, the validity of this hypothesis will be examined.

Figure 8.1: SrO Tracer in the Melter Input Stream

Figure 8.2: SrO Tracer in the Melter Output Stream Compared to a Model of Two, Well-Mixed Tanks in Series

Figure 8.3: Residuals Versus Time for a Two-Well-Mixed Tanks in Series Model of the SrO Tracer Data

Figure 8.4: Residuals Versus WPO of SrO for a Two, Well-Mixed Tanks in Series Model of the SrO Tracer Data

9.0 Effect of a Growing Feed Pile

To determine the effect of a growing feed pile on the mixing behavior of the SFCM, one turns to a comparison of the two sets of tracer data immediately following the injection of each tracer. Since no feed pile was present when the BaO tracer was first injected, and a fully developed feed pile covering approximately 95 to 98 percent of the melt surface area was present when the SrO was injected, the effect of the feed pile should be apparent from such a comparison.

Figure 9.1 shows the WPO of BaO present in the melter output stream from the start of the run ($t = 0$) up to $t = 30$ hours along with the predicted values from the TWMTIS model. Although the correlation coefficient R and the coefficient of determination R^2 indicate that the fit of the model to the data is reasonable, it is apparent that the model could be improved. For example, the standard error of regression $\sigma_{e,i}$ ranges from 39 percent of the WPO of BaO at time $t = 0$ down to 9.5 percent at time $t = 30$ hours.

Figure 9.2 shows a plot of the residuals $e_{i,j}$ calculated for the fit of the TWMTIS model to this same data. The residuals are definitely not randomly distributed about zero, which should be the case for a perfect fit ($R^2 = 1$) of the model to the data. This suggests that the model is not correctly treating the mixing in the SFCM shortly after the tracer is injected. However, it should be noted that the TWMTIS model assumes a fully developed feed pile at all times, which was not the case when the BaO was first injected. Therefore it is not surprising that the fit of the model to the data is less than perfect.

Figure 9.3 shows the WPO values of SrO in the melter output stream from the injection time ($t = 123$ hours) out to $t = 154$ hours. In this case, the feed pile was fully developed, and the SFCM was at steady-state operating conditions when the SrO was injected. Therefore the TWMTIS model of the feed pile and glass pool should match these data more closely than the BaO data. However it does not.

A comparison of the statistical measures of the fit of the TWMTIS model in Figures 9.1 and 9.3 shows that the model actually fits the BaO data slightly better than it fits the SrO data during the first 30 hours after each tracer was injected.*

The residuals $e_{i,j}$ for the SrO tracer shortly after injection are shown in Figure 9.4. They show a non-random distribution about zero with roughly the same pattern as the BaO data (cf. Figures 9.2 and 9.4).

Examination of Figures 9.1 and 9.3 suggests that the tracer data might be fitted better if the feed pile were assumed to be a plug flow region with a mean residence time of 2 to 4 hours. Physically however, the mean residence time should be roughly 7 hours, which is inconsistent with this assumption. Since some of the incoming slurry spills over the sides of the feed pile when injected by the ADS pump, the feed pile is probably not a pure plug flow region. But neither is the feed pile a pure well-mixed region, which is shown by the failure of the TWMTIS model to closely match the early portion of each tracer curve.

* The converse is true if one considers the fit to each tracer over the entire timespan of the run.

One concludes that an examination of both sets of tracer data for the first 30 hours following the injection of each tracer indicates that the **growth** of the feed pile from idling operating conditions (no feed pile) to steady-state feeding conditions (feed pile covering 95 to 98 percent of the melt surface) has no significant effect on the mixing behavior of the glass pool. This conclusion follows from a comparison of the statistical quality of the fit of the TWMTIS model to both sets of tracer data during the first 30 hours after the injection of each tracer.

Figure 9.1: BaO Tracer in the Melter Output Stream During the Early Part of the Run

Figure 9.2: Residuals Versus Time for a Two, Well-Mixed Tanks in Series Model of the BaO Tracer Data During the Early Part of the Run

Figure 9.3: SrO Tracer in the Melter Output Stream Shortly After Injection

R
E
S
I
D
U
A
L

Figure 9.4: Residuals Versus Time for a Two-Well-Mixed Tanks in Series Model of the SrO Tracer Data Shortly After Injection

10.0 Residence Time Calculations for the Crust Layer of the Feed Pile

Routt⁹ showed that the mean residence time $\bar{\tau}_i$ of the *i*th feed component injected into a glass melter by means of a positive step change in the slurry feed can be calculated as*

$$\bar{\tau}_i = \frac{\int_0^{\infty} [C_{i,o}(\infty) - C_{i,o}(\tau)] d\tau}{C_{i,o}(\infty) - C_{i,o}(0)} \quad (10-1)$$

where $C_{i,o}(\tau)$ is the concentration of the *i*th feed component in the output stream with age less than or equal to τ . Equation (10-1) applies for any type of mixing behavior as long as the input function is a positive step change in component concentration. Equation (10-1) can be used to calculate the mean residence time of the *i*th feed component in the crust layer of the feed pile as follows.

If (10-1) is written in terms of the weight percent oxide of the *i*th feed component in the crust layer of the feed pile one obtains**

$$\bar{\tau}_{i,c} = \frac{\int_0^{\infty} [WPO_{i,co}(\infty) - WPO_{i,co}(t)] dt}{WPO_{i,co}(\infty) - WPO_{i,co}(0)} \quad (10-2)$$

Using the well-mixed tank model of the crust layer of the feed pile given by (7-6), the terms in (10-2) become

$$WPO_{i,co}(\infty) = WPO_{i,sl}(\infty) W_{sl}^* \rho_{sl} f_s f_{sg} / W_{co} = WPO_{i,sl}(\infty) \quad (10-3)$$

$$WPO_{i,co}(t) = \text{eq. (7-6)} \quad (10-4)$$

$$WPO_{i,co}(0) = WPO_{i,co}(0) \quad (10-5)$$

Using (10-3) - (10-5) in (10-2) and integrating gives the mean residence time $\bar{\tau}_{i,c}$ of the *i*th component in the crust layer of the feed pile as

$$\bar{\tau}_{i,c} = \frac{f_{sg} M_c}{W_{co}} \quad (10-6)$$

Several comments about (10-6) should be made:

1. The mean residence time $\bar{\tau}_{i,c}$ is directly proportional to the mass M_c of the crust layer of the feed pile. Since M_c increases as the plenum cools (the feed pile grows in both diameter and thickness), then $\bar{\tau}_{i,c}$ will increase as one approaches steady-state operating conditions in the SFCM.
2. The mean residence time $\bar{\tau}_{i,c}$ is inversely proportional to the mass flow rate W_{co} of material emerging from the bottom of the crust layer, that is, the glass melt rate.

* Equation (3-9) from Routt⁹ with the assumption that the concentration $C_o^*(\tau)$ of "old" molecules of the tracer in the output stream is constant.

** The time t and the age τ are related by the equation $t = t_i + \tau$, where t_i is the time at which the *i*th component is injected. If $t_i = 0$, then $t = \tau$.

3. The mean residence time $\bar{\tau}_{i,c}$ is independent of the index i . If a tracer component mixes well with the glass*, then the mean residence time of the tracer must equal that of any other feed component which also mixes well.

Using data from Table 7.1, the mean residence time in the crust layer of the feed pile can be calculated from (10-6) to be

$$\boxed{\bar{\tau}_{i,c} = 7.27 \text{ hours}} \quad (10-7)$$

at steady-state operating conditions with 95 to 98 percent coverage of the melt surface by the feed pile.

If one assumes that the crust layer of the feed pile should be modeled as a plug flow region, then it can be shown that the mean residence time for the plug flow condition is also given by

$$\begin{aligned} \bar{\tau}_{i,c} (\text{plug flow}) &= \frac{f_{sg} M_c}{W_{co}} \\ &= \bar{\tau}_{i,c} (\text{well-mixed}) \quad \bullet \end{aligned} \quad (10-8)$$

For plug flow the residence time of each molecule is **equal** to the mean residence time, while for a well-mixed region there is a **distribution** of residence times about the mean residence time.

In a previous report, Routt showed that a linear variation in the mass fraction (or WPO) with depth in the crust layer leads to a mean residence time given by**

$$\begin{aligned} \bar{\tau}_{i,c} (\text{linear}) &= \frac{1}{f_{sg}(\infty) \bar{\alpha}_{crit}} \\ &= \frac{M_c}{2 f_{sg}(\infty) W_{sl}^* (\infty) \rho_{sl} f_s} \\ &= 6.05 \text{ hours} \quad \bullet \end{aligned} \quad (10-9)$$

Table 10.1 compares the predictions of different flow models for the mean residence time of the i th component in the crust layer of the feed pile. The fraction of the injected molecules that has emerged at the mean residence time is shown for each model and is related to the respective exit age distribution, which has been discussed elsewhere^{1,3}.

* This assumption will be examined elsewhere by consideration of a mass balance for each feed component used in the SF-10 run.

** From (5-11) and (7-7) of Routt¹.

Table 10.1: Comparison of Different Models of the Crust Layer		
Model	Mean Residence Time $\bar{\tau}_{t,c}$ (hrs)	Fraction Emerged at $\bar{\tau}_{t,c}$
1. Well-Mixed	7.27	0.63
2. Plug Flow	7.27	1.00
3. Linear Variation with Depth	6.05	0.63

One can conclude this section with the following observations:

1. In Section 7.0 it was shown that a somewhat better fit to the tracer data was obtained by including a well-mixed tank model of the crust layer of the feed pile with a well-mixed tank model of the glass pool. However, the effect of the feed pile is small and might also be obtained from use of another model. Pure plug flow in the crust layer would have the effect of shifting all the tracer data 7.27 hours to the right in Figures 7.1 and 8.2. This appears to be excessive. A linear (or possibly exponential) variation of WPO with depth in the crust layer might give the best fit to the data.
2. The tracer data from this run are not adequate to determine the best mixing model for the crust layer. However, the mean residence time of the i th component in the crust layer is approximately 6 to 7 hours. It is the **distribution** of residence times of individual molecules about this mean that is currently uncertain. This uncertainty should be resolved in future FACTS runs.

11.0 Residence Time Calculations for the Crust Layer and Glass Pool in Series

To determine the mean residence time of the i th feed component in both the crust layer and glass pool of the SFCM, it will be necessary to mathematically separate the tracer data into its individual components -the crust layer of the feed pile and the glass pool beneath. The effect of the slurry layer of the feed pile will be ignored since the mean residence time of molecules in this region of the melter is only 8 to 10 minutes^{2,3}.

Figure 11.1 shows the response of the crust layer to a positive step change in the i th component in the slurry feed to the melter. The mean residence time (or mean age) of a molecule in the crust layer is simply

$$\bar{\tau}_{i,c} = \frac{\int \tau_{i,c} d WPO_{i,co}}{\int d WPO_{i,co}} \quad (11-1)$$

The numerator of (11-1) is the horizontal differential area element in Figure 11.1b integrated over the area behind the curve to give the area A_1 . Thus (11-1) can be written as

$$\bar{\tau}_{i,c} = \frac{A_1}{WPO_{i,co}(\infty) - WPO_{i,co}(0)} \quad (11-2)$$

The area A_1 can also be written (using the vertical differential area in Figure 11.1b) as

$$A_1 = \int_0^{\infty} [WPO_{i,co}(\infty) - WPO_{i,co}(\tau)] d\tau \quad (11-3)$$

where the integrand is given by (7-6).

The response of the crust layer plus the glass pool is measured in the melter output stream. This response is shown in Figure 11.2a and can be calculated using (7-14). By analogy with the crust layer, one can write the mean residence time in the crust layer plus glass pool as

$$\bar{\tau}_{i,cgp} = \frac{A_2}{WPO_{i,gp}(\infty) - WPO_{i,gp}(0)} \quad (11-4)$$

where

$$A_2 = \int_0^{\infty} [WPO_{i,gp}(\infty) - WPO_{i,gp}(\tau)] d\tau \quad (11-5)$$

Figure 11.1a

Figure 11.1b

Figure 11.1: Response of the Crust Layer to a Positive Step Change in the i th Feed Component

Figure 11.2a

Figure 11.2b

Figure 11.2: Response of Both the Crust Layer and the Glass Pool to a Positive Step Change in the i th Feed Component

The mean residence time of a molecule in the glass pool can be calculated by superimposing Figures 11.1b and 11.2a as shown in Figure 11.2b. This gives

$$\begin{aligned}
 \bar{\tau}_{i,gp} &= \frac{\int \tau_{i,c} d \phi_i}{\int d \phi_i} \\
 &= \frac{A_3}{\phi_i(\infty) - \phi_i(o)_i} \\
 &= \frac{A_2 - A_1}{\phi_i(\infty) - \phi_i(o)_i} \quad \bullet
 \end{aligned} \tag{11-6}$$

where the dummy differential $d \phi_i$ is simply

$$\begin{aligned}
 d \phi_i &= d WPO_{i,co} \\
 &= d WPO_{i,gp} \quad \bullet
 \end{aligned} \tag{11-7}$$

At time $t = 0$, Figure 11.2b shows that

$$\begin{aligned}
 \phi_i(o) &= WPO_{i,co}(o) \\
 &= WPO_{i,gp}(o)
 \end{aligned} \tag{11-8}$$

and as t goes to infinity

$$\begin{aligned}
 \phi_i(\infty) &= WPO_{i,co}(\infty) \\
 &= WPO_{i,gp}(\infty)
 \end{aligned} \tag{11-9}$$

provided that losses of the i th component from the glass pool due to deposition, volatilization, and chemical reactions are all zero or negligibly small.

Equation (11-6) can now be written as

$$\begin{aligned}
 \bar{\tau}_{i,gp} &= \frac{A_2}{\phi_i(\infty) - \phi_i(o)} - \frac{A_1}{\phi_i(\infty) - \phi_i(o)} \\
 &= \frac{A_2}{WPO_{i,gp}(\infty) - WPO_{i,gp}(o)} \\
 &\quad - \frac{A_1}{WPO_{i,co}(\infty) - WPO_{i,co}(o)} \\
 &= \bar{\tau}_{i,cgp} - \bar{\tau}_{i,c} \quad \bullet
 \end{aligned} \tag{11-10}$$

Thus the mean residence time of the i th component in the crust layer plus glass pool is simply the sum of its mean residence times in each of the two regions, that is,

$$\bar{\tau}_{i,cgp} = \bar{\tau}_{i,gp} + \bar{\tau}_{i,c} \quad \bullet$$

(11-11)

More generally, (11-11) shows that the mean residence time for N mixing regions in series is simply the sum of the mean residence times for each of the regions.

Since the area A_2 in (11-10) represents the response of a well-mixed region to a positive step change (cf. Figure 11.2a), the mean residence time $\bar{\tau}_{i,cgp}$ in the crust layer and glass pool is analogous to (10-6), that is,

$$\begin{aligned}\bar{\tau}_{i,cgp} &= \frac{M_{cgp}}{W_{co}} \\ &= \frac{f_{sg} M_c + M_{gp}}{W_{co}} \quad \bullet\end{aligned}\tag{11-12}$$

Using data from Table 7.1, the mean residence time in the crust layer plus the glass pool can be determined to be

$\bar{\tau}_{i,cgp} = 68.77 \text{ hours} \quad \bullet$

(11-13)

The mean residence time $\bar{\tau}_{i,gp}$ in the glass pool beneath the feed pile can now be found by using (10-7) and (11-13) in (11-10) to obtain

$\bar{\tau}_{i,gp} = 61.5 \text{ hours} \quad \bullet$

(11-14)

The results of the mean residence time calculations are summarized in Table 11.1. The mean residence time of molecules in the slurry layer is included as well, but is dropped from the total since it is negligibly small.

Table 11.1: Mean Residence Times Calculated Using a TWMTIS Model of the SFCM

<u>Location</u>	<u>Mean Residence Time</u>	<u>% of Total</u>
1. Slurry Layer of Feed Pile	8 to 10 minutes ^{2,3}	neglect
2. Crust Layer of Feed Pile	7.27 hours	10.6
3. Glass Pool	<u>61.5 hours</u>	<u>89.4</u>
4. Total	68.77 hours	100.0

12.0 Conclusions

Equations governing glass mixing were developed and used to examine the transport of selected tracers through the SFCM during the SF-10 run. The following conclusions can be drawn:

1. Laboratory studies identified the following materials as potentially useful tracers: $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, $\text{Sr}(\text{OH})_2$, ZnO , $\text{Co}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$, and SnO_2 . Each of these materials was found to be compatible with the ATM-10-NR target glass composition at their respective glass loadings. Good analytical assay capability was demonstrated for each of these materials by use of the Induction Coupled Plasma (ICP) technique (Section 3.0).
2. Cobalt hydroxide ($\text{Co}(\text{OH})_2$) and SnO_2 were found to require additional sample preparation work in order to achieve satisfactory assay results. This will increase the labor and sample turn-around time if these materials are used as tracers (Section 3.0).
3. Glass mixing in the SFCM can be reasonably approximated by use of a single, well-mixed tank model (SWMT). However, a statistical comparison of this model to the BaO tracer data shows that this model is not completely satisfactory (Section 6.0).
4. A better model of glass mixing in the SFCM is obtained if the feed pile and the glass pool are modeled as two, well-mixed tanks in series (TWMTIS). This model gives a good fit to both the BaO and SrO tracer data. It is the best model currently available for glass mixing in the SFCM (Sections 7.0 and 8.0).
5. The effect of a fully developed feed pile on glass mixing in the SFCM is small, but not negligible. The **growth** of the feed pile from the start of the run to steady-state operating conditions has no significant effect on glass mixing (Section 9.0).
6. The mean residence time of the i th glass component in the crust layer of the feed pile is about 7.27 hours. Several models of the crust layer each give a mean residence time of 6 to 7 hours here, but are characterized by a different distribution of residence times for individual particles about the mean. Although it is intuitively attractive to consider the crust layer of the feed pile as a plug flow region, such a model requires that the SrO tracer in Figure 9.3 remain at its initial value (0.05414 WPO) until 7 hours after injection of the positive step change (until $t = 130$ hours). This is clearly not supported by the data. It is concluded that the crust layer of the feed pile is better modeled as a well-mixed region, although this model is not completely satisfactory either. This difficulty should be resolved in a future run.
7. The glass pool beneath the feed pile can be well represented as a single, well-mixed region. This means that mass transport in the x , y , and z directions is unimportant and results in considerable simplification of the general, partial differential equation (4-4), which expresses conservation of mass for the i th component in the glass pool.
8. The mean residence time in the glass pool beneath the feed pile is 61.5 hours (Section 11.0).
9. The mean residence times in the crust layer of the feed pile and the glass pool beneath the feed pile are each inversely proportional to the glass melt rate. This also applies to the mean residence time values given in Items 6 and 8 above (Section 10.0).

10. Mean residence times are additive. Therefore, the total mean residence time in the crust layer of the feed pile plus the glass pool beneath the feed pile is 68.77 hours (Section 11.0).
11. Since the equations of the TWMTIS model give good overall agreement to both the BaO and SrO tracer data, they can be used as part of the overall process model (MASBAL) for predicting glass composition in the melter output stream (or canister). When solved numerically, these equations will provide a powerful tool for predicting glass composition as a function of time and batch composition under a wide range of operating conditions. This will give WVNS a credible technique of ensuring control of glass composition as required by Section 1.1 of the Waste Acceptance Preliminary Specifications¹⁰.

13.0 Nomenclature

A_1	=	area defined by Figure 11.1b [hrs],
A_2	=	area defined by Figure 11.2a [hrs],
A_3	=	area defined by Figure 11.2b [hrs],
A_t	=	horizontal cross-sectional area of the MFHT [m^2],
$C_{i,o}$	=	concentration of the i th feed component in the melter output stream [g/l],
$\frac{d \bar{L}_{sl}}{dt}$	=	average slope of the slurry level in the MFHT over the entire SF-10 run [inches/hr],
e_j	=	measured value of the level in the MFHT at the j th time value minus the predicted value obtained by using a least squares fit to the level detector data. Also called the j th residual [inches],
$e_{i,j}$	=	measured value of the weight percent oxide of the i th feed component at the j th time value minus the corresponding calculated value predicted by either the SWMT model or the TWMTIS model. Also called the residual of the i th feed component at the j th time value,
$e_i(t)$	=	residual of the i th feed component at any arbitrary value of time,
f_s	=	mass fraction of solids in the slurry feed,
f_{sg}	=	mass fraction of the dried slurry feed that is converted into glass in the feed pile,
i	=	index used to count the number of components in the slurry feed,
I	=	maximum value of i ,
j	=	index used to count the number of time values at which the weight percent oxide of the i th component is measured,
J	=	maximum value of j ,
J_1	=	total number of measurements of the slurry level in the MFHT during the first time interval [0 - 120 hours] of the SF-10 run,
J_i	=	total number of measured values of the weight percent oxide of the i th feed component in the melter output stream,
L_{sl}	=	analytical function value of the slurry level in the MFHT at any time t [inches],

L_{sl}^*	=	least squares value of the slurry level in the MFHT at any time t [inches],
$L_{sl,j}$	=	measured value of the slurry level in the MFHT at the j th time value [inches],
$L_{sl,j}^*$	=	calculated least squares value of the slurry level in the MFHT at the j th time value [inches],
M_c	=	mass of the crust layer of the feed pile [kg],
M_{cgp}	=	mass of the dried oxides in the crust layer of the feed pile plus the mass of the glass pool beneath the feed pile [kg],
M_{gp}	=	mass of the glass pool beneath the feed pile [kg],
R	=	correlation coefficient defined as the square root of R^2 ,
R^2	=	coefficient of determination defined by (6-18),
$S_{cor,i,x}^*$	=	mass flow rate of the i th component entering the glass pool due to corrosion of the south wall of the glass pool at $x = +x^*$ [kg/hr],
$S_{cor,i,x}^*$	=	mass flow rate of the i th component entering the glass pool due to corrosion of the north wall of the glass pool at $x = -x^*$ [kg/hr],
$S_{cor,i,y}^*$	=	mass flow rate of the i th component entering the glass pool due to corrosion of the electrode and refractory on the west wall of the glass pool at $y = +y^*$ [kg/hr],
$S_{cor,i,y}^*$	=	mass flow rate of the i th component entering the glass pool due to corrosion of the electrode and refractory on the east wall of the glass pool at $y = -y^*$ [kg/hr],
$S_{cor,i}$	=	total mass flow rate of the i th component entering the glass pool from corrosion of all refractory walls and electrodes [kg/hr],
$S_{dep,i}$	=	mass flow rate of the i th component out of the glass pool due to deposition onto the melter floor [kg/hr],
$S_{og,i}$	=	mass flow rate of the i th component out of the glass pool into the off-gas system due to volatilization [kg/hr],
t	=	time [hrs],
v_x, v_y, v_z	=	glass velocity in the x , y , and z directions in the glass pool, respectively, [m/hr],
W_{sl}^*	=	volumetric slurry feed rate to the melter [l/hr],

W_{cr}	=	mass flow rate of glass emerging from the crust layer of the feed pile, that is, the melt rate [kg/hr],
W_{pour}	=	mass pour rate of glass from the melter [kg/hr],
$WPO_{i,c}$	=	weight percent oxide of the i th component inside the crust layer of the feed pile,
$WPO_{i,co}$	=	weight percent oxide of the i th component emerging from the crust layer of the feed pile,
$\overline{WPO}_{i,gp}$	=	average weight percent oxide of the i th component in the glass pool,
$WPO_{i,gp,j}$	=	measured weight percent oxide of the i th component in the glass pool at the j th time value,
$WPO^*_{i,gp,j}$	=	predicted value of the i th component in the glass pool at the j th time value as calculated by either the SWMT or the TWMTIS model,
$WPO_{i,sl}$	=	weight percent oxide of the i th component in the incoming slurry,
x	=	Cartesian coordinate pointed south in the SFCM (Figure 5.1) [m],
$x_{i,c}$	=	mass fraction of the i th component inside the crust layer of the feed pile,
$x_{i,co}$	=	mass fraction of the i th component emerging from the bottom of the crust layer of the feed pile,
$x_{i,gp}$	=	mass fraction of the i th component in the glass pool beneath the feed pile,
$x_{i,sl}$	=	mass fraction of the i th component in the slurry feed to the melter,
x^*	=	value of the x Cartesian coordinate at the glass pool boundary [m],
y	=	Cartesian coordinate pointed west in the SFCM (Figure 5.1) [m],
y^*	=	value of the y Cartesian coordinate at the glass pool boundary [m],
z	=	Cartesian coordinate pointed downward in the SFCM (Figure 5.1) [m],
z^*	=	value of the z Cartesian coordinate at the bottom of the glass pool [m],
$\bar{\alpha}_{crit}$	=	critical reaction rate constant which the i th component must exceed in order to react to completion inside the crust layer of the feed pile. Defined by (5-11) of Roult ¹ [kg/hr-kg of crust],
$\Delta x, \Delta y, \Delta z$	=	arbitrarily small increments in the x, y , and z directions [m],
Δt	=	arbitrarily small time increment [hrs],

$\alpha_{e,i}$	=	standard error of regression resulting from fitting a model to measured data for the i th feed component,
ρ_k	=	glass density in the glass pool beneath the feed pile [kg/m ³],
$\rho_{s,i}$	=	density of the slurry feed [kg/m ³],
τ	=	residence time or age of a molecule inside the SFCM [hrs],
$\bar{\tau}_{i,c}$	=	mean residence time of the i th component in the crust layer of the feed pile [hrs],
$\bar{\tau}_{i,cgp}$	=	mean residence time of the i th component in the crust layer of the feed pile plus the glass pool [hrs],
$\bar{\tau}_{i,gp}$	=	mean residence time of the i th component in the glass pool beneath the feed pile [hrs],
ϕ_i	=	dummy variable of integration defined by (11-7).

14.0 References

1. Letter OG:88:0098, K. R. Routt to Distribution, "Chemical Reactions in the Crust Layer of the Feed Pile in a Slurry Fed Glass Melter - Part I", West Valley Demonstration Project, March 25, 1988.
2. Letter OG:87:0055, K. R. Routt to Distribution, "Residence Time Calculations for Water Molecules in the Slurry Layer of the Feed Pile in a Slurry Fed Glass Melter", West Valley Demonstration Project, December 22, 1987.
3. Letter OG:88:0002, K. R. Routt to Distribution, "Residence Time Calculations for Solids in the Slurry Layer of the Feed Pile in a Slurry Fed Glass Melter", West Valley Demonstration Project, January 5, 1988.
4. Letter HG:87:0322, K. R. Routt to Distribution, "Comparison of Theoretical and Experimental Slurry Feed Rates for FACTS Run SF-9", West Valley Demonstration Project, June 15, 1987.
5. Letter HG:87:0407, K. R. Routt to Distribution, "Comparison of Theoretical and Experimental Slurry Feed Rates for FACTS Run SF-8", West Valley Demonstration Project, July 20, 1987.
6. Letter HG:87:0510, K. R. Routt to Distribution, "Comparison of Theoretical and Experimental Slurry Feed Rates for FACTS Run SF-7", West Valley Demonstration Project, September 1, 1987.
7. Montgomery, D. C. and Peck, E. A., "Introduction to Linear Regression Analysis", John Wiley and Sons, New York (1982), Chapter 2.
8. _____, "RS/1 User's Guide, Book 2, Graphics and Statistics", BBN Software Products Corporation, Cambridge, MA (1987), Section 7.4.
9. Letter OG:88:0007, K. R. Routt to Distribution, "Governing Equations for the Response of a Slurry Fed Glass Melter to a Positive or Negative Step Change in Feed Rate", West Valley Demonstration Project, January 6, 1988.
10. Kale, S. H. and Lytle, J. "Waste Acceptance Preliminary Specifications for the Defense Waste Processing Facility High-Level Waste Form", U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Washington, DC (OGR/B-8), December 1986.

DATE

FILMED

2 / 16 / 94

END