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C.J. Freeman

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

**Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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1.0 *Introduction*

Extensive research on the vitrification of certain types of high-level radioactive waste has been performed throughout the U.S. Department of Energy (DOE) complexes over the past two decades. The processes most often studied for vitrifying these wastes involve slurring the waste to make it pumpable, adding glass-forming additives, and feeding the slurry to a glass melter. The melters are typically designed to operate at temperatures exceeding 1100°C. A common vitrification system for high-level waste processing is the joule-heated ceramic melter. With this system, waste is continuously fed into a refractory-lined glass tank. The waste in the tank is heated by directly passing electrical current through the material from an immersed set of electrodes. The resulting glass product is then poured from the glass tank into cans for permanent storage.

Numerous bench-scale and pilot-scale tests have been conducted to support high-level waste vitrification projects within DOE. These projects include the Hanford Waste Vitrification Plant (HWVP), the Defense Waste Processing Facility (DWPF), and the West Valley Demonstration Project (WVDP). Testing for these projects has investigated aspects of the vitrification process such as the pumpability of the slurry feed, melter processing rates, melter scale-up, and off-gas decontamination factors for feed constituents. The high costs for testing have generated interest in using modeling to predict major processing impacts on the vitrification systems from any given feed material. Important components required for such modeling include feed composition, feed rheology, melter glass temperature, melter geometry, and melter power configurations.¹ Some work has already been performed in modeling glass melters, but little attention has been given to feed composition (Routt 1982).

To address the need for data on melter feed composition in melter modeling, the work reported here first investigated the major operating parameters for previously tested slurry-fed, joule-heated, vitrification systems. Next, the slurry feed rate was modeled, using an energy balance, for the melt transition region within these systems. The required inputs to this energy balance were then obtained to estimate melter feed rates. Finally, this modeling was evaluated by making melter performance estimates based on changes in the major input parameters.

¹ Elliott, M.L. et al. "Preliminary Studies of Vitrification Rate Enhancement," Pacific Northwest Laboratory, December 1989.

2.0 Previous Data for High-Level Waste Vitrification Testing

2.1 Previous Melter Performances

To attempt to characterize melter performance, melter operating information was obtained for a number of Pacific Northwest Laboratory (PNL) slurry-fed vitrification tests performed in recent years. The melters used for the tests included the high-bay ceramic melter (HBCM)², the pilot-scale ceramic melter (PSCM)^{3,4,5,6,7,8,9,10} and the liquid-fed ceramic melter (LFCM) (Bjorklund et al. 1982). The test information accumulated consisted of data for power, feed rate, and slurry oxide concentration versus run time. This information was taken only for steady operation (steady feed rate) periods during each test. In order to obtain melter performance information, the data for each melter test was plotted as the mass feed rate of the slurry material versus melter power. This plot is shown in Figure 2.1.

The plot trends in Figure 2.1 suggest a linear dependence for the mass feed rate of slurry on melter power. This dependence is expected since the slope of a linear regression through any one data set should be inversely proportional to the melting enthalpy of the material. In addition to enthalpy information, the x-axis intercept from a linear regression should indicate the total melter power losses at a feed rate of zero for that particular melter. These losses are due to melter-specific design factors such as heat losses to water-cooling jackets, air contact surfaces, in leakage air (off-gas), etc. Note that simply measuring the idling (no slurry feeding) power of a melter would not account for the insulative contributions of a transitional feed layer on top of the glass pool as well as other processing effects. Therefore, the idling power of a melter would not necessarily match the minimum melter power predictions from Figure 2.1.

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- 2 Buchmiller, W.C. et al. "High Bay Ceramic Melter Experiment Summary Report: HWVP-13/HBCM-86-2," 7H35-86-12/HLV1B, Pacific Northwest Laboratory, June 1986.
 - 3 Sevigny, G.J. et al. "PSCM-3 Summary Report," Pacific Northwest Laboratory, October 1981.
 - 4 Dierks, R.D. et al. "PSCM-5 Summary Report," Pacific Northwest Laboratory, March 1982.
 - 5 Sevigny, G.J. et al. "PSCM-6 Summary Report," Pacific Northwest Laboratory, October 1982.
 - 6 Perez, J.M. et al. "PSCM-11, HWVP-5 Test Report," Pacific Northwest Laboratory, January 1983.
 - 7 Perez, J.M. et al. "West Valley Waste Vitrification Experiment: PSCM-15 Summary," Pacific Northwest Laboratory, September 1983.
 - 8 Peterson, M.E. et al. "Hanford Waste Vitrification Program: PSCM-17 Summary," Pacific Northwest Laboratory, November 1984.
 - 9 Perez, J.M. et al. "West Valley Pilot-Scale Melter Experiment: PSCM-19/19E Run Summary," Pacific Northwest Laboratory, January 1985.
 - 10 Peterson, M.E. et al. "Pilot-Scale Ceramic Melter, Nonradioactive Experiment No. 20 (PSCM-20) Summary Report," Pacific Northwest Laboratory, June 1985.

Figure 2.1 Performance Curves of Previous PNL Melter Runs

The empirical melting enthalpy and minimum melter power loss information for each of the data sets in Figure 2.1 were obtained through linear regressions of the data in the manner described previously. These results are shown in Table 2.1.

Table 2.1 Tabulated Melter Performance Data from Figure 2.1

PNL Melter System	Waste Slurry Type	Test ID Number(s) in Data Set	Melter Surface Area (m ²)	r Squared of Linear Regression	Total Feed Enthalpy Calculated from Slope (J/g slurry)	Minimum Melter Power Calculated from x-Intercept (kW)
HBCM	HWVP	1, 2	0.25	0.91	2475 ± 802	5 ± 4
PSCM	DWPF	3, 4, 6	0.73	1.00	3277 ± 1	9 ± 0
PSCM	WVDP	9, 11, 15, 16, 19, 20	0.73	0.75	3390 ± 1964	21 ± 22
PSCM	HWVP	17, 22	0.73	0.99	4789 ± 511	6 ± 7
LFCM	DWPF	4, 5, 6, 7	1.05	0.92	2384 ± 722	125 ± 50
LFCM	HWVP	8	1.05	0.94	2697 ± 77	83 ± 2

Error analysis information is given for each value shown in Table 2.1. The largest enthalpy error is that for the PSCM (WVDP feed) data set. This error is largely due to individual tests in which differing slurry-solids concentrations were used. The water/solids content of a certain

feed type will greatly determine the corresponding melting enthalpy of the material. Therefore, the differences in concentration for each melter test contribute to the scatter of the data. Additionally, the inherent changes in the bulk glass temperature with changes in system power also affect the estimated melting enthalpy. However, these changes are minimal compared to the effects of slurry concentration for the information shown in Table 2.1 since bulk glass temperatures generally targeted $1150^{\circ}\text{C} \pm 25^{\circ}\text{C}$ for each of these tests.

As described previously, the minimum melter power values shown in Table 2.1 correspond to the power losses for that specific melter, excluding the power used to melt the feed material. These values give some idea of the efficiency of the melter itself. For example, each of the PSCM data sets shown were obtained from a relatively unchanged vitrification system. Therefore, the minimum melter power estimates from each PSCM data set should be the same for each feed type, with the slope of the data sets differing due to the different thermal characteristics of each feed material. Indeed, the minimum melter power estimates for each PSCM data set are within the error ranges of one another, approximately 9 kW.

Unlike the PSCM data set, the two LFCM data sets show major differences in their predicted minimum melter power estimates. These differences are due to significant design changes made to this melter prior to the LFCM-8 test. A sloped bottom was added to the melter, which provided more melter cavity refractory and insulation. The plenum heaters were also changed from two nichrome wire panel heaters to a bank of horizontal silicon carbide heaters. This change was accompanied by changes in the lid insulation, which significantly reduced the amount of heat loss. As a result of these changes, Table 2.1 shows a reduction in melter power losses, from the previous LFCM tests, of approximately 42 kW.

An interesting aspect of the minimum melter power estimates is shown by the differences stemming from the use of plenum heaters. The PSCM-5 data point, identified in Figure 2.1, was the only PSCM test on the plot which involved the use of plenum heaters. These heaters produced a greater processing rate and a greater total melter power requirement. However, not all of the extra power from the plenum heaters was used to melt the feed material. If this were the case, the PSCM-5 point would have fallen on a linear regression of the other data. Therefore, these additional losses were estimated by using the slope of the rest of the PSCM/DWPF data set on the PSCM-5 point to predict the minimum melter power estimate with plenum heaters. This value is approximately 50 kW, 40 kW greater than the minimum melter power calculated without plenum heaters. Most of this additional lost power went into heating the melter off-gas to a higher temperature. This suggests that melt rate boosting may

be more efficiently performed by increasing the power input through the melter electrodes, not to the plenum heaters. The HWVP has recently taken this approach by studying a melter capable of operating at higher temperatures, thus allowing more power input to the melter electrodes.

2.2 LFCM-8 Melter Performance

For the purposes of modeling melt rate, the LFCM-8 test was selected as the modeling case since adequate amounts of feed slurry from this test were available for required lab analyses and testing. The LFCM-8 processing results were given in Figure 2.1. As already described, these data points were taken from steady operation segments within the LFCM-8 test. These operating segments are defined as those run-time periods which had a constant melter feed rate. A plot of the LFCM-8 slurry feed rate over the course of the test is shown in Figure 2.2. The steady processing segments are identified on the plot with arrows. The higher feed rate segment in the middle occurred when more melter electrode input power was attained during operation because of an erroneous glass temperature measurement.

Figure 2.2 LFCM-8 Slurry Feed Rate Versus Run Time

The average total power consumption for the LFCM-8 test was 142 ± 10 kW. The average distributions of this input power were determined from the test data and are shown in Figure 2.3. This data was comprised of direct electrical line power information to the melter

electrodes, plenum heaters and discharge heaters. The input power distribution shows that approximately equal amounts of power went to the melter electrodes and the plenum heaters.

Figure 2.3 Distribution of Average LFCM-8 Melter Power Input (142 ± 10 kW)

The corresponding outputs of the system power, shown in Figure 2.3, were also estimated using the LFCM-8 test data. This data included off-gas flowrates and temperatures, plenum temperatures, cooling jacket water flows and temperature increases, and feed slurry flowrates and concentrations. The results of the output power distribution calculations are shown in Figure 2.4. The feed water and steam power consumptions were calculated using the measured water content and flow rate of the feed slurry. The feed solids power consumption estimate was based upon calorimetry data which will be discussed in section 5.2.

Figure 2.4 shows that the majority of the system power (39%) was absorbed by heat losses to the cooling jackets, melter lid, and discharge section. A large amount of power was also consumed by the off-gas sweep air, which attained an average temperature of 281°C during the test. This heat loss estimate constituted approximately 20% of the system power. The power required to elevate the water vapor from the feed slurry to the melter plenum temperatures (average of 653°C) was approximately 11% of the total system power. The melter plenum heaters undoubtedly supplied the greatest portion of the power, which heated the sweep air and the slurry water vapor, supporting some the plenum heater inefficiencies discussed previously. The final 30% of the system power was used to actually melt the feed slurry. This power resulted in an average glass temperature of 1163°C for the test.

Figure 2.4 Distribution of Average LFCM-8 Melter Power Output (142 ± 10 kW)

3.0 Theoretical

The previous section described how specific efficiency data were determined for a number of slurry-fed glass melters, more specifically for the LFCM as that melter was used for its eighth test. The purpose of identifying this information is so that a more detailed study of a certain feed material can be used to yield relative performance impacts to these known vitrification systems. Therefore, the next step was to model the melt transition area within the melter where dominating physical traits of a feed material have the greatest impacts upon the material's melt rate.

3.1 *Energy Balance of Melter Cold Cap*

The vitrification systems discussed in section 2.0 operated by continuously pumping slurried waste simulant and glass-forming materials directly on top of the molten glass pool. At steady conditions this feeding process produces a transitional layer, referred to as a cold cap, which

often covers most of the glass surface. The following diagram illustrates the general formation of the melter cold cap during steady operation.

Figure 3.1 Simplified View of a Slurry-Fed Melter Cold Cap

At steady processing conditions, a liquid slurry pool usually forms on the surface of the cold cap. Depending on the melter and processing conditions, slurry pools that cover most of the cold cap can form with a slurry-fed melter. Slurry pool areas can often be difficult to quantify from a top view since the slurried material often fingers into unseen pockets within the hardened cold cap crust regions.

To understand the dominant factors influencing the melting rate of a slurry, an energy balance was used on the system described in Figure 3.1. In order to help simplify this system only the area directly under the slurry pool was modeled. This initial approach was taken since the LFCM-8 testing showed large slurry pool coverages and the cold cap crust layers outside of the slurry pool appeared non-dynamic, as if mostly providing an insulative covering. Using this approach, the region directly under the slurry pool can be considered a one-dimensional, steady-state heat transfer problem through a flowing material. The second-order differential equation which explains the thermal behavior of this problem is shown as follows (Kays and Crawford 1987):

$$\dot{m}C_p \frac{\delta T}{\delta x} - kA \frac{\delta^2 T}{\delta x^2} = 0$$

This equation is valid when mass flow rate ($\dot{m}$), heat capacity (C_p), thermal conductivity (k), and area (A) are constant with temperature (T) and material thickness (x). Unfortunately, the thermal conductivity and heat capacity values for melter slurries are typically very temperature dependent. To address this temperature dependence, the cold cap can be represented as a number of thin stacked slices for which the thermal conductivity and heat capacity of each slice is approximately constant over its corresponding temperature range, much like a finite element analysis. This approach is depicted in Figure 3.2.

Figure 3.2 Cold Cap Layers of Constant Thermal Conductivity and Heat Capacity

To obtain the solution to the second-order differential equation shown above, boundary conditions must be determined for each of the individual cold cap layers. The first layer can be represented as the layer directly on top of the glass surface. Hence, an input power (q_{in}) from the glass into this layer can be set initially. This boundary condition comes directly from Fourier's equation and is shown as follows:

$$-k_1 A \frac{dT}{dx} = q_{in} \quad (\text{at } \Delta x_1 = 0)$$

Since the temperature of the first layer, right at the glass surface, should be equal to the average glass temperature below it, the second boundary condition can be written as follows:

$$T = T_{glass} \quad (\text{at } \Delta x_1 = 0)$$

Using these boundary conditions with the governing differential equation, shown previously, will reveal the thermal solution for the first cold cap layer. This solution is shown as follows:

$$T = T_{glass} + \frac{q_{in}}{\dot{m}Cp_1} (1 - e^{-\beta_1 \Delta x}) \quad \text{Where } \beta_1 = -\frac{\dot{m}Cp_1}{k_1 A}$$

For a constant ΔT , the previous solution can be manipulated to generate the corresponding thickness of the first layer (Δx_1). This solution is shown as follows:

$$\Delta x_1 = \frac{k_1 A}{\dot{m}Cp_1} \ln \left(\frac{\dot{m}Cp_1}{q_{in}} (\Delta T_1) + 1 \right)$$

An approach similar to the one above can be used to solve the thermal equations for each of the other cold cap layers. However, the boundary conditions will change based on the results of the corresponding previous layer. The first boundary condition is shown as follows, for any layer n :

$$-k_n A \frac{dT}{dx} = q_{in} e^{\left(-\sum_{z=1}^{(z=n-1)} \beta_z \Delta x_z \right)} \quad (\text{at } \Delta x_n = 0)$$

The second boundary condition simply uses the closest temperature of the previous layer for the zero thickness temperature of the layer in question. When using a constant ΔT to define each layer, this boundary condition, for any layer n , becomes:

$$T = T_{glass} - (n - 1)(\Delta T) \quad (\text{at } \Delta x_n = 0)$$

Thus, when incorporating these boundary conditions the corresponding layer thickness solution can be written as follows, for all but the first layer:

$$\Delta x_n = \frac{k_n A}{\dot{m}Cp_n} \ln \left(\frac{\dot{m}Cp_n}{q_{in}} e^{\left(\sum_{z=1}^{(z=n-1)} \beta_z \Delta x_z \right)} (\Delta T_n) + 1 \right)$$

The previously derived equations were manipulated to give layer thicknesses so that thermal information, such as thermal conductivity and heat capacity, could be entered for constant temperature intervals (over which these properties are approximately constant) throughout the entire temperature range experienced by the melter feed material. Forcing these individual

layer thicknesses to sum to a known total cold cap thickness allows an iterative solution of mass feed rate to be determined. Hence, the mass feed rate can be modified until all of the cold cap layer thicknesses sum to a total cold cap thickness target value. Such a target value can be obtained from specific melter run information.

3.2 Sensitivity of Energy Balance Parameters

The previous energy balance approach to estimating a feed rate value uses a number of input parameters. To establish the impacts of these parameters on feed rate estimates, a sensitivity analysis was performed on each using the equations presented previously. A 210-layer scenario was used with a corresponding temperature increment of 5°C. Individual input parameters were changed while holding the remaining input parameters constant, and the corresponding changes in the calculated feed rate were recorded. There were some differences in the sensitivities of certain parameters, depending upon which constants were used for the remaining input parameters. Therefore, a number of sensitivities were obtained for different constant sets and an average sensitivity was calculated. The results of this analysis are shown in Table 3.1.

Table 3.1 Sensitivity of Energy Balance Parameters on Estimated Feed Rate

Model Parameter Name	% Change in Calculated Feed Rate Over % Change in Parameter
Slurry pool area (A)	0.95
Average thermal conductivity ($\bar{k}$)	1.01
Total cold cap thickness ($\sum_{z=1}^{z=n} \Delta x_z$)	1.07
Average heat capacity ($\bar{C}_p$)	0.51

As shown in Table 3.1, all of the main heat balance parameters significantly affect the estimated feed rate. The average heat capacity showed less of an affect on the estimated feed rate than did the other parameters, suggesting that the heat transfer parameters are the most crucial in the energy balance. Such a result is plausible when considering the amount of energy which can penetrate straight through the cold cap and into the plenum space when the cold cap is thin enough and/or the thermal conductivity is high enough.

4.0 *Experimental Analyses*

As has been described, performing even a simplified melter cold cap energy balance requires the temperature-dependent thermal conductivities and heat capacities of the feed material in question as inputs. Therefore, this information was obtained for the LFCM-8 feed material. The thermal conductivities were measured in an apparatus constructed and operated at PNL, and the heat capacity information was obtained from differential scanning calorimetry analyses of the feed material (Thomason and Wilburn 1960).

4.1 *Equipment for the Thermal Conductivity Measurements*

The assembly used for the thermal conductivity measurement is shown in Figure 4.1.

Figure 4.1 Thermal Conductivity Measurement Device

The purpose of this equipment was to impose a temperature gradient across a long crucible filled with dried feed material. The temperatures could then be measured along the length of the material for a given amount of transferred power. This power is determined by holding a water-cooled heat sink at one end of the gradient and measuring the water flow rate and corresponding temperature change. All of this information can then be used to calculate the thermal conductivity of the feed material as a function of temperature.

The crucible was composed of mullite, with an inner diameter of 3-1/16 inches and an overall length of 12 inches. The bottom 1-1/2 inches of the crucible was exposed to the furnace environment, with the remaining portion surrounded by an alumina-based insulation to minimize radial heat losses. The top of the crucible was sealed with a water-cooled copper lid to provide the cold side of the temperature gradient across the material. This lid was doughnut shaped, with an outer diameter of 3-1/4 inches and a height of 1 inch. A 1 inch center hole was required for the thermocouple assembly to penetrate the lid and the sample material. This lid was fabricated from 1/8 inch copper plate and water flow was routed through 1/4 inch copper tubing.

To monitor the thermal gradients throughout the material, four type S thermocouples were used. These thermocouples were placed 2 inches apart, in the vertical direction, within the slurry. The thermocouples had exposed element junctions and were sheathed with 1/4 inch outer diameter mullite tubes. The ceramic sheaths minimized the vertical heat transfer that would have occurred with metal-sheathed thermocouples. The temperature information used to calculate the amount of heat transferred through the material was collected using two type J thermocouples. These thermocouples monitored the inlet and outlet temperatures from the water-cooled lid. Additionally, the flow rate of the water was measured with a 0 to 1.5 gpm rotameter.

All of the temperature data measured was stored in a data acquisition computer designed for acquiring the data and simultaneously logging it into history files. A 486 AT personal computer was used with a data acquisition software package called Cim-Pac™. The personal computer linked hardware was used to read the thermocouple signals was a Dutec™ multichannel analog/digital (I/O) Plexer board. The data acquisition system allowed attending test personnel to observe the temperature trends and identify when steady heat transfer was achieved.

4.2 DTA/DSC Equipment Description

Differential thermal analysis (DTA) works on the principle of heating a given sample and a thermally inert reference material at a given heating rate and measuring the temperature differences between the two materials. The corresponding endothermic and exothermic behavior of a sample can be represented by these measured temperature differences. Differential scanning calorimetry (DSC) works on this same basic principle; however, DSC uses more complex and accurate reference and calibration data such that quantitative calorimetric information can be obtained (Wendlant 1986).

The temperature dependent heat capacity of the LFCM-8 feed material was measured by the Chemical Engineering Department of Washington State University. The instrument used for these measurements was a Perkin Elmer DTA-7 Differential Thermal Analysis unit capable of running in DSC mode. The DTA-7 is rated for a temperature range from room temperature to 1700°C (Wendlant 1986). The instrument was calibrated using high purity indium, aluminum, and gold standards. A known mass of each of these standards was heated to its melting temperature and the heat of fusion was measured and corrected for, using the known value of the standards. These three calibration standards were selected for calibrating over the full analysis range for the melter feed (room temperature to 1150°C) since their respective melting temperatures are 167, 660, and 1064°C.

5.0 Experimental Results

5.1 Thermal Conductivity Measurements

The thermal conductivity measurements were performed with the LFCM-8 feed material using the apparatus described in section 4.1. Feed slurry was added to the crucible and the crucible was placed in a drying oven at 95 to 98°C for 1 to 2 days. Once the slurry had dried more slurry was added to compensate for the volume reduction, and the new slurry was dried. This process was repeated until the crucible was completely filled with dried material. The thermocouple assembly was placed in the crucible before the slurry additions began so that it would not have to be inserted through the hardened feed.

Once the crucible was prepared, it was placed in the furnace apparatus and fitted with the water-cooled plug (see Figure 4.1). The furnace was then turned on and the water cooling was

started. Incremental temperatures were obtained across the thermocouples within the feed material by adjusting both the furnace temperature and the water cooling flow rate. The gradient temperatures were not recorded until they reached steady values over time. Table 5.1 shows the thermal gradients imposed on the material as well as the heat sink data and corresponding calculated thermal conductivities.

Table 5.1 Measured Data for Thermal Conductivity Calculations

Temperatures Between Thermocouples (C)	Distance Between Thermocouples (cm)	Cooling Water Temp. Increase (C)	Cooling Water Flow Rate (ml/min)	Calculated Thermal Cond. (W/m K)
57 to 363	5.1	12	15.8	0.46
142 to 672	5.1	8	15.9	0.18
191 to 772	5.1	10	15.8	0.20
363 to 848	5.1	12	15.8	0.29

The data in this table shows that the maximum temperature for any of the thermal gradients was less than 850°C. Higher temperatures than this were not attempted since glass phase transitions would begin to occur and the resulting voids would interfere with the thermal conductivity measurements. For each of the temperature ranges shown in Table 5.1, the cooling water flow rates were adjusted such that the cooling water temperature increased by approximately 10°C. This adjustment ensured that there was sufficient accuracy in the measured transferred power to calculate the thermal conductivity.

In order to manipulate the thermal conductivities, shown in Table 5.1, into a more defined temperature-dependent thermal conductivity series, the temperature ranges for each measurement were divided into individual segments. These segments were defined as each of the possible temperature increments within all of the data. For example, the first temperature segment was 57 to 142°C, followed by 142 to 191°C, then 191 to 363°C, and so on. Next, an array of equations were developed such that the average thermal conductivity for each of these segments could be determined. The criteria for these equations were that the respective individual segment thermal conductivities added to the multisegment thermal conductivities shown in Table 5.1.

To solve the previously described equation matrix, the thermal conductivity for the fourth temperature segment was determined by averaging the middle temperature range thermal conductivities listed in Table 5.1. This approach was applied because of the relatively constant thermal conductivity observed in these two temperature ranges. The resulting thermal conductivity temperature dependence is plotted in Figure 5.1. This plot shows the calculated average thermal conductivities for each temperature segment as well as a superimposed, smoothed plot of the same information.

Figure 5.1 Temperature-Dependent Thermal Conductivity for Dried LFCM-8 Material

The plot shown in the figure shows a low range of thermal conductivity encountered between 300 and 500°C. The highest temperature segment (800°C range) thermal conductivity was determined to be approximately 0.7 W/m K. These thermal conductivity values fall into the ranges expected for clay or ceramic type materials for these temperature ranges (Bennett and Myers 1982).

The thermal conductivity versus temperature set shown in Figure 5.1 was used in the feed rate prediction equations described in section 3.0. However, this data was still incomplete for temperatures between 850 and 1150°C. Therefore, a thermal conductivity versus temperature relationship, developed by Elliott for HWVP glasses from a compilation of literature values, was used for this higher temperature range.¹¹ This relationship is given as follows:

¹¹ Internal PNL letter from M.L. Elliott to C.C. Chapinan, "Windows for Physical Properties Used in Freeze Valve Mode," September 27, 1988.

$$k \text{ (W/m K)} = 7.47 - 1.32 \times 10^{-2} T + 7.30 \times 10^{-6} T^2 \quad (\text{for approximately 900 to 1400 K})$$

This relationship yields a thermal conductivity of 2.5 W/m K at 1000°C. Multicomponent silica-based glasses have been reported to attain thermal conductivities in the 2.9 to 3.8 W/m K range (Volf 1984). Therefore, the thermal conductivity predicted from the relationship shown above is close to the expected range for multicomponent glasses, such as the HWVP waste glass product.

5.2 DTA/DSC Heat Capacity Measurements

To measure the temperature-dependent heat capacity, a three-step process was used.¹² First, a DSC sample holder was filled with a known amount of alumina powder and heated in the DTA-7 unit at a predetermined temperature ramp rate. The alumina was used in each run to keep the emissivity from the top of the sample holder as constant as possible. Next, the same sample holder was emptied of the alumina then partially filled with a known mass of sapphire powder. The original mass of alumina powder was then placed back on top of the sapphire, again to retain consistency in the emissivity, and the holder was run again in the DTA-7 at the previous temperature ramp. Once these two sets of data were collected, the published temperature-dependent heat capacity for sapphire was used to back out the heat capacity interferences of the sample holder and alumina powder. Finally, an analysis was performed with a known mass of dried LFCM-8 feed material in the sample holder covered with the same mass of alumina. Once this sample was analyzed, the sample holder and alumina interferences were backed out, leaving the heat capacity for the dried LCFM-8 feed material only. Data plots of each of the three calorimetry steps, just described, are shown in Figure 5.2.

¹²

Communication with Colin Williams, Product Specialist, Perkin-Elmer Co., August 1993.

Figure 5.2 DTA/DSC Curves Measured for LFCM-8 Feed Thermal Analysis (200°C/hr)

The final weight of the LFCM-8 feed sample, after it was analyzed by the DTA-7, was used with the calorimetry data and the temperature ramp data to calculate the temperature-dependent heat capacity of the material. A plot of this heat capacity data is shown in Figure 5.3.

Figure 5.3 Heat Capacity for Dried LFCM-8 Feed Material

Although the data in Figure 5.3 is described as only the heat capacity of the LFCM-8 feed material, it actually encompasses the whole field of thermal data. This includes heats of fusion, heats of vaporization, and endothermic and exothermic reactions, as well as heat capacity. By integrating the data in Figure 5.3 with respect to temperature, the dried feed enthalpy versus temperature can be obtained. This enthalpy information is shown in Figure 5.4.

Figure 5.4 Enthalpy for Dried LFCM-8 Feed Material Versus Temperature

By representing the heat capacity information as enthalpy data, one can better understand the total amount of energy required to bring the dried feed material to any given temperature. Furthermore, known thermal data for water can now be added to compensate for analyzing just the dry feed material. One benefit for splitting out the solid and water thermal data is that the amount of water in the feed can be varied mathematically for the feed rate analyses. This equates to being able to vary the oxide loading of the feed during the feed rate estimations. Figure 5.5 shows the combined water thermal data and dried LFCM-8 calorimetry data for a slurry of 447 grams oxide per liter, which was the average slurry oxide loading for the LFCM-8 melter test.

Figure 5.5 Enthalpy for LFCM-8 Feed (447 g_{oxide}/liter) from DSC and Water Data

Because of equipment difficulties the calorimetry data for the LFCM-8 feed material could be accurately analyzed only to 900°C. However, some uncorrected data from the same material indicated little change in the heat capacity between 900 and 1200°C, since most of the phase transitions and chemical reactions occurred below this temperature range. Therefore, for the purposes of melt rate estimations, the feed enthalpy was extrapolated to 1150°C based on the 850 to 900°C range data. Nevertheless, Figure 5.5 shows that the bulk of the energy consumed by the feed goes into vaporizing the water portion of the slurry.

Figure 5.5 shows the total feed melting enthalpy to be approximately 1850 J/g_{slurry}. The LFCM-8 test performance data calculation for heat capacity, shown previously in Table 2.1, was 2697±77 J/g_{slurry}. The approximately 850 J/g_{slurry} difference between these two values can be attributed to the energy used to heat the vaporized slurry water to high-temperature steam in the melter plenum. The energy required to produce this steam can be calculated using power distribution information shown in section 2.2 and the average feed rate of LFCM-8 test. This value is approximately 740 J/g_{slurry}. This steam power consumption was based on slurry water flow and average plenum temperatures. Therefore, the associated error of this value could account for the remaining difference between the two enthalpies. The differences in bulk glass temperature can also impact the melting enthalpy. However, as shown in Figure 5.5, a 50°C change in glass temperature would result only in a difference in the melting enthalpy of approximately 35 J/g_{slurry}.

5.3 *Kinetic Limiting Factors*

In addition to the DSC/DTA studies, which yielded melter feed heat capacity information, measurements were made of any kinetic limiting reactions within the feed material. If a melter feed were composed of large amounts of material that reacts at a rate slower than the desired melter feed rate, the kinetics of this reaction would limit the melter processing rate according to those kinetics (Taylor and Rowan 1983; Gistling and Fradkina 1952). The experimental approach taken to try and identify any such limitations was to first determine the range of cold cap residence times typically observed for a joule-heated melter about the size of the LFCM. This residence time range was determined from cold cap tracer studies performed during previous vitrification tests. Next, calorimetric information was measured by the DTA-7 for dried LFCM-8 feed material at heating schedules corresponding to these cold cap residence time ranges. Certain peaks from each heating schedule analysis were then compared to see if reaction kinetic shifting could be observed.

The results of this study showed apparent peak shifting with changes in the heating schedule. The average peak temperatures decreased with a decreasing heating rate. However, this phenomenon was reported to be largely a result of heat transfer limitations within the DTA/DSC sample (Wendlant 1986). As a result, this approach for determining kinetic limitations proved to be ineffective for the present melt rate investigation. Other kinetic measurement methods, such as differential x-ray diffraction, may prove more effective for obtaining the rate-limiting information. As a result, discrete feed rate limitations due to kinetic limitations were not determined for the LFCM-8 feed.

6.0 *Energy Balance Feed Rate Predictions*

6.1 *LFCM-8 Results Comparison*

The energy balance methodology discussed in section 3.0 was used in conjunction with known LFCM-8 processing values and the measured feed properties to estimate slurry processing rates under varying conditions. The total number of cold cap model layers used for the energy balance was 210. This total number of layers and a temperature range of 100 to 1150°C, resulted in a temperature interval for each layer of 5°C. The measured thermal conductivity and heat capacity data, discussed previously, was used for this modeling. This data was manipulated to give constant values for the 5°C temperature interval.

Table 6.1 shows the measured processing information obtained for the LFCM-8 melter test. Each of the values in the quantitative category were measured during the LFCM-8 test with high degrees of confidence. The average power transferred into the feed material was determined from the calorimetry data. Using this data, the average power to melt the feed material was 40 kW for the LFCM-8 test. This can be determined by simply dividing the measured total enthalpy for melting the slurry by the mass feed rate. Even though cold cap thicknesses and slurry pool coverages were recorded during the test, these values were considered qualitative since they were based on operator observations from limited view ports on the melter lid.

Table 6.1 Measured LFCM-8 Processing Information

<u>Quantitative LFCM-8 Processing Information:</u>	
Melter Surface Area =	1.05 square meters
Average Cold Cap Coverage =	89 %
Average Slurry Oxide Concentration =	447 g oxide/liter
Average Slurry Feed Rate =	58 liters/hour
Power Transferred into Feed Material (Calorimetry) =	40 kW
<u>Qualitative LFCM-8 Processing Information:</u>	
Slurry Pool Coverage of Cold Cap =	20 to 30 %
Cold Cap Thickness =	2 to 5 centimeters

Initially all of the information shown in Table 6.1, except average slurry feed rate, was used in the energy balance model to predict an average slurry feed rate. However, the operator observed values for slurry pool area and cold cap thickness limited the total estimated power transfer into the system to 8 kW. Since the calorimetry based power requirement of the feed slurry was 40 kW it suggested that these qualitative values were far from the actual slurry pool area and cold cap thickness in the LFCM-8 test. As a result, a range of melter processing rates were calculated, using the energy balance model, for a number of cold cap thicknesses and slurry pool coverages in order to better define these parameters.

In order to analyze the results of this exercise the governing energy balance equation, from section 3.1, was used to normalize the relevant terms. This equation is shown as follows:

$$\Delta x_n = \frac{k_n A}{\dot{m} C p_n} \ln \left(\frac{\dot{m} C p_n}{q_{in}} e^{\left(\sum_{z=1}^{(z=n-1)} \beta_z \Delta x_z \right)} (\Delta T_n) + 1 \right)$$

By only considering the pertinent terms in the above equation; cold cap thickness (x), slurry pool area (A), slurry mass flow rate (m), and transferred power (q), the approximate dependency between these terms can be determined. By dividing the cold cap thickness by the slurry pool area and plotting this term against the inverse mass flowrate multiplied by the log of the mass flow rate over the power, the above equation suggests an approximate linear dependency. Therefore, the results of the energy balance model predictions with varying slurry pool area and cold cap thickness were placed in this format and plotted in Figure 6.1.

Figure 6.1 Model Results of Cold Cap Thickness and Slurry Pool Area versus LFCM-8 Processing Rates

Figure 6.1 shows the linear dependence predicted by the above equation. The vertical dashed line in this figure shows the x-axis point which corresponds to the processing information shown in Table 6.1. This point results in an energy balance model prediction of approximately 0.006 m^{-1} for cold cap thickness over slurry pool area. By using the qualitative data, shown in

Table 6.1, a comparative value of 0.03 m^{-1} can be calculated. The model predicted value of 0.006 m^{-1} could correspond to a slurry pool coverage and a cold cap thickness combination of 85% and 2 cm, respectively.

The larger slurry pool coverage estimate substantiates some of the reported observations of the LFCM-8 cold cap. A probing of the cold cap during this run showed liquid slurry pockets underneath a hardened crust very near the outside edge of the cold cap. This top crust was most likely caused by the plenum heaters in the melter head space. Since these pockets of liquid slurry could not be seen from a top view, the slurry pool coverage could very well have covered much of the total cold cap area. Additionally, the energy balance prediction accounts for the surface roughness of the hardened material beneath the slurry pool which could produce a greater "effective" slurry pool area. The operator observed cold cap thicknesses could have also been high due to this crust on top of areas of the slurry pool.

In order to further describe the model predicted cold cap characteristics, the cold cap thickness over slurry pool area prediction of 0.006 m^{-1} was used to generate the predicted temperature distribution through the cold cap. The calculated thickness for each individual cold cap layer was plotted against temperature. The resulting temperature profile is shown in Figure 6.2 for the LFCM-8 cold cap energy balance fit.

Figure 6.2 Predicted Temperature Profile through Cold Cap underneath Slurry Pool

The cold cap temperature profile shows the bulk of the temperature gradients occurring within the half of a centimeter directly below the slurry pool. This configuration is typical for a material in direct contact with a heat sink, like the cold cap slurry pool. The higher thermal conductivities, used for the material at temperatures above 900°C, also contributed to the steep profile at those higher temperatures.

6.2 Processing Rate Dependencies on Slurry Oxide Concentration

The next step in the energy balance analysis was to use the findings in section 6.1 as "baseline" information and show relative changes in the LFCM-8 feed rate predictions with varying processing parameters. The first parameter varied was the slurry oxide concentration. This parameter was modified and predicted glass production rate changes were observed. The slurry oxide concentration impacts the melting enthalpy of the slurry material since it determines the amount of water in the material. Once the slurry oxide concentration was changed in the energy balance, the input power was modified such that the power was completely transferred into the feed material. The results of this exercise are shown in Figure 6.3.

Figure 6.3 Glass Production Rate Dependency on Slurry Oxide Concentration

This figure shows that the predicted glass production rate increases linearly with slurry oxide concentration for the LFCM-8 feed. Furthermore, the slope of the curve is proportional to the average volumetric slurry feed rate in liters per second. Therefore, the data suggests that the

volumetric slurry feed rate should be relatively constant for the slurry oxide concentration range investigated.

In addition to the predicted glass production rates for the LFCM, the results from the HBCM-2 test were also included in Figure 6.3. This test measured production rates of HWVP feed material at 415, 515, and 654 grams oxide per liter slurry concentrations. As shown in Figure 6.3, the glass production rate increased between the first two oxide concentrations, then decreased at the highest slurry concentration. These results were attributed to the rheological behavior of the slurry, as the 654 grams oxide per liter slurry was reported to be quite thick and produced a pile-shaped slurry pool. Nevertheless, Figure 6.3 shows a similar trend between the LFCM-8 predictions and the results for the first two HBCM-2 oxide concentrations. These two slurry concentrations were reported to have fewer rheology problems than the highest concentration in the HBCM-2 testing. The difference between the two data sets is due to the inaccuracies of using melter surface area normalizing for glass production rate estimations, as well as some slight differences between the two HWVP feed compositions.

The glass production rate dependency on slurry rheology shows some of the problems with using a simplified geometry energy balance for melt rate predictions. Hence, ensuring that the feed rheology behavior is within known processing ranges is crucial for the validity of the feed rate predictions. Establishing the rheology ensures that the cold cap and resulting slurry pool are flexible and well distributed across the glass surface, as depicted previously in Figure 3.1. Additionally, ensuring that the feed rheology falls within set process ability ranges also ensures that the feed material can be pumped through the feed preparation and transfer systems in the full-scale vitrification plant.

6.3 Processing Rate Dependencies on Glass Temperature

The next process rate-dependent parameter varied in the energy balance model of the LFCM-8 feed material was the bulk glass temperature. To perform these model estimations, the heat capacities of the LFCM-8 feed material were extrapolated to 1250°C. LFCM processing rates were then estimated using the parameters shown in Table 6.1. The results of this investigation are shown in Figure 6.4.

Figure 6.4 Glass Production Rate Dependency on Glass Temperature

As seen in this figure, the calculated feed rates are linearly dependent upon bulk glass temperature. This dependency is due to the constant heat capacity values used for the feed material at the upper temperature ranges. As mentioned previously, this constant heat capacity was observed with DSC/DTA for the LFCM-8 feed material at the temperatures displayed in Figure 6.4, but could not be used to calculate heat capacities for that material due to instrumentation problems above 900°C.

In addition to the predicted data, actual LFCM-8 run data is shown in Figure 6.4. The first few points of this data appear to follow the predicted trends for feed rate. However, the highest feed rate/temperature point in the figure had to be represented by a range. This data representation was used since the precise glass temperature at this feed rate was unknown, although it did exceed 1200°C. This high temperature segment occurred when the glass thermocouples within the melter failed and gave lower than actual readings. The glass temperature was not expected to have exceeded 1250°C since these temperatures would have resulted in the meltdown of the LFCM electrode material. Nevertheless, the comparisons in Figure 6.4 suggest that this high LFCM processing rate corresponded to a bulk glass temperature near 1250°C.

7.0 *Conclusions and Recommendations*

An energy balance model has been developed that takes into consideration primary parameters of slurry-fed glass melter processing, such as slurry oxide loading and glass temperature, in order to predict melter feed rate. The glass temperature dependency is important since higher temperature ($>1500^{\circ}\text{C}$) melters are being investigated for increasing waste processing rates. A simple data analysis, like the one described for the LFCM-8 feed, could be performed (at higher temperatures) on proposed high-temperature melter feeds to predict feed rate performance. The cold cap parameters of slurry pool area and cold cap thickness were shown to be extremely qualitative parameters as they are presently being measured. Although these parameters can be determined by baselining with an actual melter run, better methods of their measurement would be much more desirable. Slurry rheology was shown to be unaccounted for in the model when the spreadability of a slurry over the cold cap was inhibited. Fortunately, slurry materials which exhibit these types of rheological problems are not typically pursued for processing in any vitrification system, simply because of mass transport problems.

In addition to the energy balance predictions of processing rate, melter efficiencies, like those shown in Table 2.1, can be used to predict a total power requirement from the vitrification system being studied. Note that this efficiency information may be obtainable for nonexistent systems which are in the design stage only. This would involve a complete thermal analysis of the system. Although rate-limiting kinetics were not identified for the LFCM-8 feed, the investigation of other analytical methods for doing this may prove effective. This phenomenon may or may not prove to be a concern for most waste slurry types. A flowsheet of the recommended melt rate model approach is shown in Figure 7.1.

Figure 7.1 Flowsheet of Proposed Feed Rate Prediction Process

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