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NUCLEAR WASTE GLASS

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Melting of Foaming Batches: Nuclear Waste Glass

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Abstract. A simple model is presented for the rate of melting of a batch blanket in an electric glassmelting furnace. The melting process is assumed to be jointly controlled by the heat transfer from the pool of molten glass and the batch-to-glass conversion kinetics. Factors affecting the melting rate in the conversion-controlled regime are discussed. Attention is paid to gas evolution from redox reactions in waste glass batches and component accumulation within the blanket. It is suggested that the high rate of the blanket-free melting in a mechanically agitated furnace is made possible by increasing the rate of melt surface renewal.

INTRODUCTION

In an electric glassmelting furnace, the thermal boundary layer thickness, which depends on the temperature and velocity fields within the melt in the region under the batch blanket, can be controlled by furnace design, electrode position, or installation of bubblers. Glass processing technology has been dominated over the last several decades by an effort to optimize these elements. This effort has been only partially successful in increasing melting rates because, as will be shown below, melting becomes conversion-controlled when the heat transfer rate is high. Since the conversion process is complex and simulation of batch blanket conditions in the laboratory is difficult, the conversion process in the batch blanket is not as well understood as the heat transfer and flow in molten glass. So far, only the fundamentals of batch-to-glass conversion have been developed - see Hrma [1], Schill [2-4], and Bickford et al. [5]. This paper deals with the limitation of enhancing the melting rate by increasing the heat transfer. In this connection, batches evolving gas at melting temperatures (foaming batches) and batches exhibiting component accumulation are discussed and the mechanism of blanket formation is suggested.

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THEORY

The melting rate (N) is defined as the mass of glass produced in a time unit at a unit surface area of the batch blanket. For one-dimensional steady-state melting, the melting rate is related to the heat flux (q) coming from the pool of molten glass by

$$N = q/Q, \quad (1)$$

where Q is the heat per unit mass of glass to be delivered through the blanket bottom, including the conversion heat, the sensible heat, and the heat exchange through the upper surface of the blanket.

The heat flux passing through the blanket bottom can be expressed either as the incoming heat from the molten glass,

$$q = \lambda_1(T_1 - T_2)/\delta_1, \quad (2)$$

or the heat entering the blanket,

$$q = \lambda_2(T_2 - T_3)/\delta_2, \quad (3)$$

where λ_1 and λ_2 are the effective heat conductivities of the molten glass and the conversion layer, T_1 is the maximum temperature of the melt, T_2 the batch blanket bottom temperature, T_3 the temperature at which the terminal conversion process begins, δ_1 the thermal boundary layer thickness, and δ_2 the conversion layer thickness. The conversion layer thickness can be determined as $\delta_2 = v/k$, where k is the reaction rate coefficient for the terminal batch conversion process and v is the batch velocity. The terminal conversion process, which can be dissolution of refractory grains or evolution of gas by redox reactions, is that process which for a particular batch determines the blanket bottom. The batch velocity is related to the melting rate by $v = N/\rho$, where ρ is the batch density. Hence, $\delta_2 = N/k\rho$. Obviously, with a faster reaction (larger k), a thinner layer is needed. On the other hand, if the melting rate is higher, the batch moves more quickly and requires a thicker layer to complete conversion.

By equations (1) and (3), the blanket bottom temperature is:

$$T_2 = T_3 + N^2 Q / \lambda_2 k \rho. \quad (4)$$

Hence, the blanket bottom temperature increases as the melting rate increases. If the melting rate is low, the batch passes through the blanket slowly, its temperature increases slowly, and it is exposed to low temperatures for a long time. This allows conversion to be completed at a low temperature. If the melting rate is high, the batch is heated rapidly, spends a shorter time at lower temperatures, reaches higher temperatures with a low extent of conversion, and the temperature at which the process is completed is high. The blanket bottom temperature grows, by equation (4), with the square of the melting rate, because T_2 increases with both the heat flux and batch velocity, which are both proportional to N .

By equations (1) and (2), the melting rate is $N = \lambda_1 (T_1 - T_2) / \delta_1 Q$. If the temperatures T_1 and T_2 were fixed, then $N \rightarrow \infty$ as $\delta_1 \rightarrow 0$. But since T_2 increases as N increases, the difference $T_1 - T_2$ approaches zero as T_2 approaches T_1 . This restricts the growth of N . Eliminating T_2 from equations (1), (2), and (4), one obtains

$$N = (1/2)(N_C^2 / N_H) [\sqrt{1 + 4N_H^2 / N_C^2} - 1], \quad (5)$$

where

$$N_C = \sqrt{[\lambda_2 (T_1 - T_3) k \rho / Q]} \quad (6)$$

is the ultimate melting rate achievable by enhancing heat transfer without changing the conversion kinetics and

$$N_H = \lambda_1 (T_1 - T_3) / \delta_1 Q. \quad (7)$$

The melting rate is conversion controlled ($N \rightarrow N_C$) if the conversion rate is low ($k \rightarrow 0$) or the heat transfer rate is high ($\delta_1 \rightarrow 0$). Under these circumstances, the melting rate is determined by the physical and chemical characteristics of the conversion layer and is no longer affected by the pool conditions, except for the melting

temperature. Moreover, the blanket bottom temperature approaches the melting temperature ($T_2 \rightarrow T_1$), which follows from eliminating q and δ_2 from equations (1) and (3) and comparing the result with equation (6). Conversely, if the conversion rate is high ($k \rightarrow \infty$) or the heat transfer rate from the melt pool is low ($\delta_1 \rightarrow \infty$), the melting rate is controlled by heat transfer ($N \rightarrow N_H$) and the conversion process is completed within a narrow temperature span ($T_2 \rightarrow T_3$). As is illustrated in Fig.1, which displays equation (5) in terms of normalized variables, the melting rate is controlled by heat transfer if $N_H/N_C \ll 1$, by conversion if $N_H/N_C \gg 1$, and jointly controlled in the intermediate regime.

DISCUSSION

Heat-transfer-controlled melting was typical in the early stages of the development of glassmelting furnaces. As this development approaches the limits of possible heat transfer enhancement, the

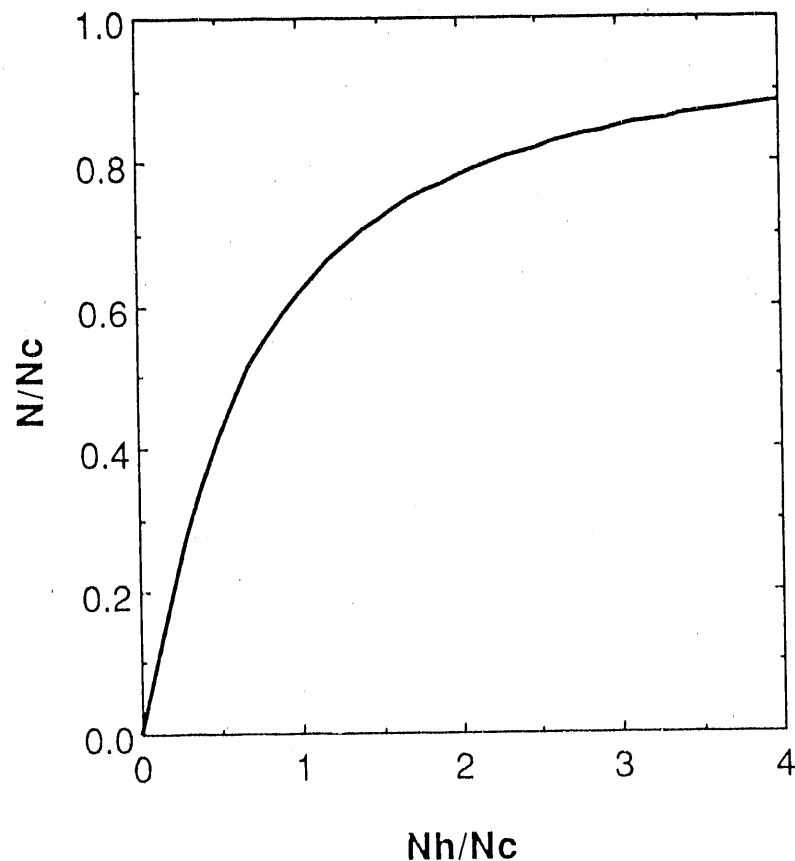


Fig. 1. Effect of conversion rate on melting rate.

melting rate is controlled by the conversion kinetics. Consequently, a further increase in melting rate can be achieved by increasing N_C . N_C can be increased by increasing the heat conductivity and density of the conversion layer, by raising the maximum temperature in the furnace, by enhancing the conversion rate, by lowering the conversion heat (or by supplying more heat from above), or by decreasing the temperature at which conversion starts (see equation (6)). Since the batch properties depend on temperature, temperature also has important indirect effects on the melting rate.

Density. The batch can expand in volume several times during melting by accumulating gases [5-7]. This has a direct negative effect on melting rate as expressed by equation (6). Increased porosity affects other batch properties, such as heat conductivity.

Heat conductivity. At lower temperatures, at which the radiative heat transfer is insignificant, heat is conducted in a porous material predominantly by the condensed phase, which consists of solid particles and melt. The presence of melt increases heat conductivity by increasing the contact area between solid particles. At higher temperatures, the radiative transfer contributes to the overall heat transfer within the material [8,9].

Maximum melting temperature. Raising temperature is the most effective way to increase the melting rate, both directly and by the temperature effect on ρ , k , and α . Since T_2 is close to T_1 in the conversion-controlled regime, the heat conductivity and conversion rate attain their highest possible values in this regime. Unfortunately, the maximum temperature is limited by the corrosion of the refractory walls and the electrodes and by volatilization from the portions of the melt surface that are not covered by batch.

Conversion rate. The terminal process (i.e., the dissolution of refractory particles in melt or bubble growth) is affected by the chemical form of raw materials, grain size of raw materials, and temperature [10,11].

In multicomponent batches, the refractory and flux components are separated by the less-reactive components. Separate prereacting of a limited number of raw materials removes this "dilution" effect. Hence, an obvious melting enhancing method is to replace refractory oxides, such as Al_2O_3 , ZrO_2 , or ZnO , with their more reactive compounds, such as nepheline, zircon, or willemite [12,13]. Components other than refractory materials can be replaced by those which react with the refractory constituents more readily: for example, sodium hydroxide exhibits higher reactivity with silica than sodium carbonate [14], which is more reactive than sodium sulfate [15]. The early melting reactions significantly affect the terminal process by generating primary melts, consuming refractory grains, affecting the composition of the melt surrounding these grains, and releasing gases before they can be trapped within the glassforming melt. Minor additions, such as inorganic salts with low melting points, increase the initial reaction rates [16,17] and, if they remain in the form of a phase-separated melt, facilitate gas removal and prevent sintering of refractory particles [6].

Large refractory grains take a long time to dissolve. With fine grains, if their agglomeration is prevented, conversion can be completed at reduced temperatures [18]. However, this may cause fining problems because the viscosity of silica-rich glass is high. If the fine grains dissolve at low temperatures, bubbles can be trapped in the melt; the refining agents may not function because the fining process may require the presence of solid particles for bubble nucleation. Therefore, batches with fine refractory grains must be heated rapidly to keep viscosity low.

Minimum temperature. The lowest temperature at which the conversion process proceeds at a measurable rate (T_3) can be decreased by selecting more reactive raw materials, employing minor additions, or using fine-grained materials. The minimum temperature also depends on the heating rate, increasing as the heating rate increases.

Conversion heat. Heating the blanket from above in the form of preheated batch or upper heating, or producing exothermal reactions

within the blanket, reduces Q , thus enhancing the melting rate. However, exothermic reactions (such as oxidation of sucrose by nitrates [9]) may produce undesirable effects leading to the melting rate reduction. Using cullet or frit instead of raw materials diminishes energy requirements, but cullet produces a high-viscosity melt at low temperatures and separates raw materials that would otherwise react with each other [19].

Foaming batches. Waste glass batches frequently contain multivalent oxides, such as Fe_2O_3/FeO . Their shift towards the reduced form with increasing temperature [7,20] is accompanied by the evolution of oxygen. Even a small shift in the redox ratio produces a large volume of gas if the concentration of the oxide is high. This leads to the formation of a bubbly layer under the batch blanket (foam), which may significantly decrease the melting rate. Addition of carbon can reduce multivalent oxides before the gas can be trapped within the melt. For example, a mixture of Fe_2O_3 and carbon completely reacts by 470 C [21,22]. However, in the presence of other components that dilute the reactants, the reaction is slow and remains incomplete even at the maximum melting temperature [5].

Component accumulation. Some batches are prone to component accumulation within the blanket. Accumulation of minor constituents whose role is to enhance the melting rate is beneficial. These constituents evaporate in lower parts of the blanket and condense in the upper portions, where their concentration becomes higher than that in the batch as charged [23].

Detrimental accumulation effects are produced by generation of low-viscosity melts that drain between the refractory particles leaving them without a sufficient amount of fluxes to dissolve in [24]. These particles may sinter into a crust under which gas accumulates, separating the particles from the drained fluxes. Also, when the melt becomes continuous, buoyancy or flotation by gas bubbles may cause the undissolved refractory particles to accumulate at the top portion of the melt [25], where they cannot dissolve if their concentration becomes higher than the solubility limit.

Free-surface melting. The main cause of a low conversion rate is the blanket itself. If the presence of the blanket in the glassmelting furnace can be eliminated (if volatilization is not of a concern), the rate of melting can increase by an order of magnitude.

Consider an idling melt pool of a uniform temperature. If batch charging begins at a low rate, the batch is almost instantaneously heated to the pool temperature and melts without forming a continuous blanket. Although the free convection will tend to recover the heat loss, an increase in the charging rate will bring about a decrease of the pool surface temperature. This will lead to a reduction of the batch-to-glass conversion rate until some batch will remain floating on the melt surface. This will happen when $N > N_{crit.}$, where $N_{crit.}$ is the critical charging rate. Eventually, the pool surface will be covered by a fully developed blanket. Because of the non-slip condition, it is more difficult to deliver the convective heat to a floating batch than to the free surface. Hence, the blanket, once formed, tends to persist.

Since most of the melting heat is delivered by convection, the value of $N_{crit.}$ depends on the melt surface renewal rate. If the melt surface is renewed by free convection, then $N_{crit.} \ll N_C$. If the melt is agitated, the surface renewal rate increases far above the level allowed by free convection and $N_{crit.} \gg N_C$. As has been demonstrated by Richards [26,27], a high critical charging rate can be achieved if agitation is preventing the formation of the blanket.

Rapid melting requires fine refractory grains. If the lifetime of the batch is longer than its residence time on the melt surface, the batch is pulled down into the pool by the impeller and the conversion is completed below the melt surface. This may lead to a bubbly melt. Moreover, large particles may lead to stony glass because of the short residence time of the glass in the melter. If the batch melting time is short, which requires fine grains, all melting reactions can be completed at the surface and batch gases are released directly into the atmosphere.

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