INCREASING HIGH-LEVEL WASTE LOADING IN GLASS WITHOUT CHANGING THE BASELINE MELTER TECHNOLOGY

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ABSTRACT

The main factors that determine the cost of high-level waste (HLW) vitrification are the waste loading (which determines the volume of glass) and the melting rate. Product quality should be the only factor determining the waste loading while melter design should provide a rapid melting technology. In reality, the current HLW melters are slow in glass-production rate and are subjected to operational risks that require waste loading to be kept far below its intrinsic level. One of the constraints that decrease waste loading is the liquidus-temperature limit. Close inspection reveals that this constraint is probably too severe, even for the current technology. The purpose of the liquidus-temperature constraint is to prevent solids from settling on the melter bottom. It appears that some limited settling would neither interfere with melter operation nor shorten its lifetime and that the rate of settling can be greatly reduced if only small crystals are allowed to form. Thus the liquidus temperature constraint may be too restrictive considering the cost associated with low waste loading. Investigating this matter requires realistic mathematical modeling of the melter that includes the behavior of solid particles suspended in the melt. Modeling calls for accurate data regarding the dynamics of nucleation, growth, and dissolution of solid particles within the temperature and velocity fields of glass in the melter. This paper provides a preliminary estimate of the rate of settling for spinel crystals in HLW glass, shows the impact of minor components in glass on the size of spinel crystals, and presents the mass-transfer coefficient, as a function of temperature, for the growth and dissolution of spinel crystals. The mechanism of crystal growth and dissolution during settling is briefly discussed. The main result of the study is that it is possible to increase waste loading even with the existing technology if the crystallinity constraint were formulated in accordance with the chemistry and physics of the generation and behavior of the suspended solid phase. The outcome of the melter model is described in a separate report.

INTRODUCTION

Precipitation of crystalline material in the high-level waste (HLW) glass melter is considered undesirable (1). Crystals have generally a higher density than molten glass. Spinel, the most common crystalline material in HLW glass, is nearly twice as dense as melt. When settling, solids form sludge that grows on the melter bottom. A growing layer of sludge will eventually obstruct the flow of glass from the melter, causing serious melter-operation problems that can lead to a premature melter shutdown. To prevent crystalline material from forming in the melter, glassmakers impose an upper limit on the liquidus temperature of glass (currently 1050°C).[a]

HLW glass must comply with several processing and product-acceptability constraints. Processing constraints limit viscosity, electrical conductivity, and liquidus temperature of molten glass. The waste loading, defined as the mass fraction of waste components in the glass, can be increased until one of the constraints cannot be met with any combination of glass-forming and glass-modifying additives. With property-composition relationships in a mathematical form, the highest waste loading that is compatible with the property constraints can be determined numerically for any tank-waste composition.

To understand how constraints work, we could conduct an experiment in which we melt the waste with a pre-melted mix of additives, called frit. Melting pure waste would probably violate all the constraints. As we add more and more frit to the waste, all constraints may eventually be met. When the last property is within its prescribed limits, the corresponding frit addition determines the maximum waste loading for this particular frit. If we use a frit of a different composition, we reach a higher or lower maximum waste loading than in the previous case. This is because individual frit components differently affect the properties of the resulting waste glass. An optimum frit composition would yield higher waste loading than any other frit. This optimum depends on waste composition and property constraints used.

Alternatively, we may add to the waste individual additive components instead of pre-melting them into a frit. The obvious choice for the first component to be added is silica. Adding just enough silica to convert the waste into glass will achieve a high waste loading, but the temperature required for melting the glass is likely to be much higher than that which the melter can tolerate. To decrease the melting temperature, we may chose to add an alkali oxide, say Li_2O. If we add enough Li_2O to reach the desired melting temperature (that is, the desired viscosity at the melter operating temperature), we may find that the glass is non-durable. This can be fixed by adding boron oxide. The last problem we might face is the presence of a large number of spinel crystals in the melt at temperatures above 1050°C. To take care of this, we have no choice but to increase the content of all the additives (in different proportions) until the crystals are dissolved.

In many cases, we would discover that without the crystallinity constraint (i.e., the restricted liquidus temperature), the waste glass would meet the other constraints with a substantially higher waste loading. This will happen when HLW contains iron and nickel. In molten glass, iron and nickel react, forming spinel as the primary solid phase (chromium and manganese are also common spinel components). Thus the waste loading of spinel-forming wastes is usually limited by liquidus temperature. Without this constraint, waste loading is likely to be limited by the product acceptability constraint. The viscosity constraint is less likely to limit waste loading, and the electrical-conductivity constraint is nearly impossible to be violated with HLW compositions at Hanford and Savannah River as long as product acceptability and viscosity constraints are met.

The experiments described above were performed by Fini and Hrma (2) and Bailey and Hrma (3,4). Fini and Hrma (2) found that for a Hanford neutralized acid waste, the liquidus temperature limited waste loading to less than 34 mass%, whereas the chemical-durability constraint allowed waste loading as high as 70 mass% if liquidus temperature was unconstrained. In a later study, Bailey and Hrma (3,4) showed that 75 mass% waste loading was possible for the all-blend Hanford waste if no processing constraint were applied (only silica was added to the waste). Even though the highest waste loading would be 5 to 10 mass% lower in the large-scale melter than in a laboratory crucible, these examples show that the liquidus-temperature constraint is restrictive and costly (a 1% increase in the waste loading can save approximately 500 million US dollars at Hanford [1]).

This economic incentive provides motivation for finding ways of increasing waste loading without putting melters at risk. Advanced melters may not be limited by liquidus temperature because the melting temperature is sufficiently high or the solid phase is effectively removed from the melter. An alternative is to replace the current *ad hoc* 1050°C liquidus-temperature limit with a constraint based on the understanding of spinel behavior in the melter. How much sludge can be tolerated without causing melter-operation problems? Can the crystal size be decreased to slow down settling? Can the sludge be removed or dissolved? Is the sludge electrically conductive? Our experimental and modeling work indicates that an increase in waste loading is possible and can be accomplished with or without changes in the current vitrification technology. This paper summarizes the main results that support this assertion.

PRELIMINARY ESTIMATES

The rate of the sludge-layer growth at the melter bottom is a function of the spinel crystal size. The settling velocity of cubic crystals suspended in molten glass (u) can be estimated using the modified Stokes law:

$$u = k_{hind} \frac{\Delta r g a^2}{h} \qquad \text{(Eq. 1)}$$

where Dr is the difference between the crystal density and the melt density, g is the acceleration due to gravity, a is the crystal size, h is the melt viscosity, and k_{hind} is the coefficient for hindered settling. Hindered settling occurs when a large number of interacting particles are settling instead of just one particle as in the original Stokes formula (5). Using the values 2.7×10^3 kg/m^3 for glass density, 5.2×10^3 kg/m^3 for spinel density, 10 Pa·s for melt viscosity, and 0.0405 for k_{hind} (this value is based on direct observation of spinel settling in MS-7 baseline glass [6]), we obtain $u = k_u a^2$ with k_u = 99.3 $m^{-1}s^{-1}$. The rate of growth of the sludge layer is

$$U = uv_G / v_S \qquad \text{(Eq. 2)}$$

where v_G and v_S are the spinel volume fraction in glass and in sludge, respectively. With the values listed above, we have, for the typical HLW glass melter, $U = 3.13a^2 v_G/v_S$ with U in mm/year and a in µm.

Based on samples from experimental melter runs, spinel sludge contains 15 to 30 mass% spinel. The corresponding approximate volume fraction is $v_S = 0.1$. Taking 1 mass%[b] for spinel concentration in glass, we get $v_G = 0.005$. Using these values and combining Equations (1) and (2), we obtain U = 0.16 mm/year for a =1 µm and U = 15.7 mm/year for a =10 µm.

Suppose U ≤ 10 mm/year is an acceptable limit (the actual value would depend on melter design, safety margin, and the length of melter campaign) and suppose $v_S = 0.1$ (20 mass%) is a reasonable estimate for spinel fraction in sludge (this fraction increases with aging). To meet this condition, crystals must be smaller than 8 µm if $v_G = 0.005$ (1 mass%). Alternatively, spinel volume fraction in melt must be smaller than 0.003 (0.6 mass%) if the crystals are 10 µm in size.

It follows from these preliminary calculations that 1-µm crystals create less than a 1-mm sludge layer per year. If the crystal size increases to 10 µm, the growth rate of the sludge layer increases to 16 mm per year. These calculations indicate that the melter may not be put to a significant risk of blockage if spinel crystals are small enough. However, these calculations neglect many important features of glass processing. Therefore, they do not constitute complete evidence. Only a more accurate and detailed analysis can help us understand how the complex velocity and temperature fields in the melter and the complex thermodynamics and kinetics of the growth and dissolution of spinel crystals in molten glass affect the rate of sludge formation.

MODELING THE GLASS MELTING PROCESS

Mathematical modeling is an excellent tool for analyzing the hydrodynamics, heat transfer, mass transfer, and melt chemistry in a pool of molten glass. Mathematical modeling has been well established for commercial glass furnaces. The main challenge from HLW processing is extending these modeling techniques to assess the nonlinear response of solid or gaseous inclusions to the physical fields, mainly to velocity and temperature distributions. The first mathematical model that successfully responded to this challenge is described elsewhere in these proceedings (7).

Mathematical modeling helps us understand an extremely complex process of mutually interacting fields in a HLW glass melter. In the case of an electrically heated glass melter, the electric field in molten glass is produced by the electric potential differences on the electrodes. This process is coupled with the temperature field because the electrical conductivity of the melt depends on the temperature, and the electric current generates heat. The temperature field is coupled with the velocity field because hot glass tends to move upward, bringing the heat needed for the melting to the feed, which floats, as a cold cap, on the top of the melt. However, melt density and other glass properties (viscosity, thermal conductivity, and electrical conductivity) depend not only on temperature, but also on the concentration of solid particles (such as spinel crystals) and gas bubbles.

The gravity field maintains convective currents in the melt due to the density differences. Solid and gaseous particles grow and dissolve according to the local temperature and concentration. Moreover, they are subjected to their own buoyant motion within the melt. This motion depends on the density difference between the melt and the particle and on the particle size. The size distribution of particles or bubbles changes from point to point within the melt. Some solid particles reach the melter bottom and create a layer of sludge. Most of the gas bubbles reach the top surface of the melt, where they burst or create a layer of foam.

The complex interactions between temperature, velocity, electric potential, and concentration fields within the melt are mathematically described in the form of mutually coupled partial differential equations. These equations are solved for a set of boundary conditions that describe the melter design and operation.

Apart from obtaining a more accurate assessment of the sludge formation rate, mathematical modeling can quickly assess the effect of melter design and operation parameters on spinel behavior. This can save years and millions of dollars in melter testing. With mathematical modeling, experimental melter runs can be planned more effectively, and their data can be extended to a wider range of parameters. Additionally, mathematical modeling provides an inexpensive and rapidly responding tool for evaluating design and operation changes targeted to achieve a substantial increase in the rate of melting. The increase in melting rate is important for the production efficiency and the energy efficiency of any glass melter, including low-activity waste glass melters as well as industrial glass melters, whether heated by electricity or fossil fuel.

Mathematical modeling can only be successful if it is based on complete and accurate values of material parameters. These include the properties of the melt, the crystals, and their mixture as functions of temperature, glass composition, the concentration of crystals, crystal size, and their mutual interaction (7).

THERMOKINETICS OF SPINEL IN MOLTEN GLASS

The following thermokinetic data of spinel in molten HLW glass were measured to provide parameters for mathematical modeling:

- the basic material parameters for the glass
- the rate of crystal nucleation, equilibrium concentration, the size and number density, the rate of growth and dissolution, and the rate and mode of settling, all as functions of temperature (6,8)
- crystal equilibrium concentration, crystal size, and crystal number density as functions of glass composition (9)
- the relationship between the oxygen partial pressure and spinel formation (10)
- spinel sludge structure and rheology (11)
- the response of spinel crystals to the temperature histories simulating the melter environment (12).

One of the highlights of the experimental research completed thus far is the evidence that the crystal nucleation density can vary from less than 10 crystals per mm^3 to more than 10^5 crystals per mm^3, depending on the presence and concentration of nucleation agents in the waste glass feed. This span in the number density corresponds to the average crystal size from 80 μm to 3 μm. Figure 1 shows the effect of minor component additions to a simplified HLW baseline glass (MS-7) of 11 components. Some of the platinoid nucleation agents, such as Ru, are minor components in HLW streams. Moreover, Cr, a minor HLW component and a major spinel component, acts itself as a nucleation agent. It is not as effective as noble metals, yet it increases the number density of crystals by an order of magnitude and thus effectively decreases the crystal size. This may be of interest for the waste streams with a high concentration of Cr. Because Cr strongly increases liquidus temperature, its presence would greatly reduce waste loading. This, however, may not be necessary, considering that Cr has little effect on spinel concentration below liquidus and produces small crystals [9].

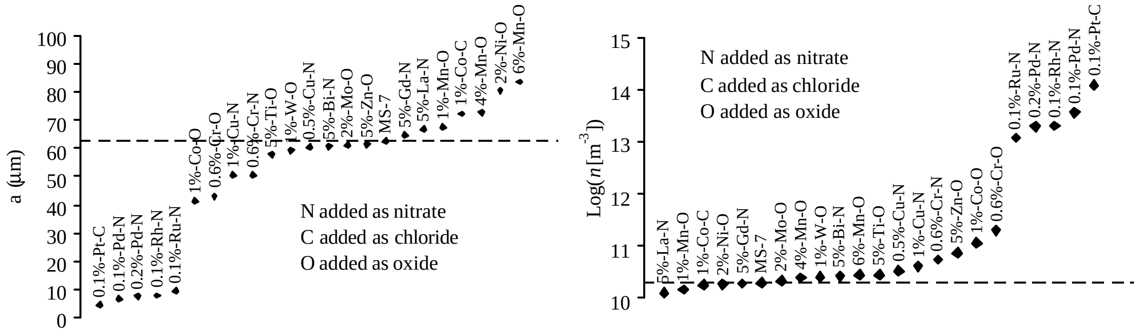

Fig. 1. Effect of Minor Component addition to MS-7 Glass on the Average Spinel Crystal Size (*a*) and the Number Density of Spinel Crystals (*n*). The numbers at data points represent mass% of oxides added to the glass. Minor components were batched as nitrates (N), chlorides (C), and oxides (O). The dashed line represents the value for glass without an addition.

To study the behavior of spinel crystals, we used MS-7 glass (13) with the liquidus temperature of 1078°C (see [7] for other properties of this glass). For crystal growth, we first heat-treated the melt at 1200°C and then cooled it to a constant temperature (in the range of 750°C to 1070°C), at which we kept the glass for varying amounts of time. In quenched samples, we measured the size of individual crystals with an image analyzer.

For dissolution experiments, we used a similar technique, except that after the initial pre-heat at 1200°C, the glass was heat treated at 900°C to develop crystals that were then subjected to dissolution at a constant temperature in the range of 1050°C to 1200°C.

The main purpose of the study was to provide constitutive equations and values of material parameters in these equations to be used in mathematical models that simulate the hydrodynamics, thermodynamics, and kinetics of HLW glass processing in the melter. For the growth and dissolution of spinel crystals, we used the Hixson-Crowell (HC) equation that has been established for dissolving silica grains in commercial glass (14). The HC equation is directly related to Fick's law of diffusion, allows accounting for convective effects, and is sensitive to the crystal number density, which is the decisive factor for the effect of spinel settling on melter operation and lifetime. The HC equation has a single kinetic parameter, the mass-transfer coefficient (k), applicable to both dissolution and growth of crystals. In its differential form, the HC equation reads

$$\frac{da}{dt} = 2k(V_0 - na^3) \qquad \text{(Eq. 3)}$$

where a is the crystal size, t is time, V_0 is the equilibrium volume fraction of crystals in melt, and n is the crystal number density.

The crystal-number density corresponds to the rate of nucleation. Fortunately, nucleation of spinel is virtually instantaneous, and the incubation time for crystallization is close to zero [13]. This considerably simplifies the matter for the mathematical modeling of melters where the temperature of each material point of glass changes rapidly. At the first approximation, the crystal-number density can be considered a function of temperature and glass composition (13) (especially the concentration of nucleation agents), see Figure 2. The equilibrium size of crystals is a function of the equilibrium concentration of spinel, a function of temperature and glass composition (13,15).

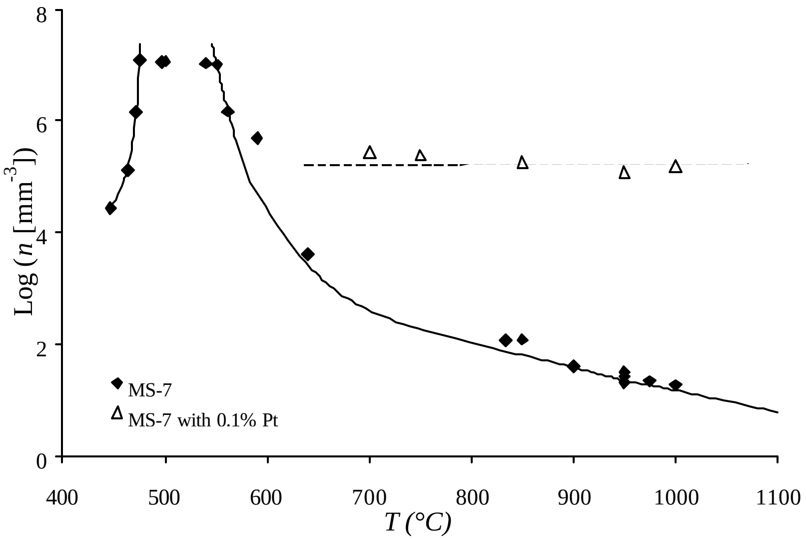

Fig. 2. Number Density of Spinel Crystals as a Function of Temperature (MS-7 Glass)

The mass-transfer coefficient for spinel in MS-7 glass is plotted in Figure 3 as a function of inverse temperature. The line shows that the same function can be used for both growth and dissolution as a first approximation. Nevertheless, the data indicate that dissolution could be somewhat slower than growth and that enhanced dissolution occurred at higher temperatures. Crystals grew before they could dissolve. Their growth produced a nonuniform concentration field around them, which could affect subsequent dissolution. Convective effects could accelerate dissolution at higher temperatures.

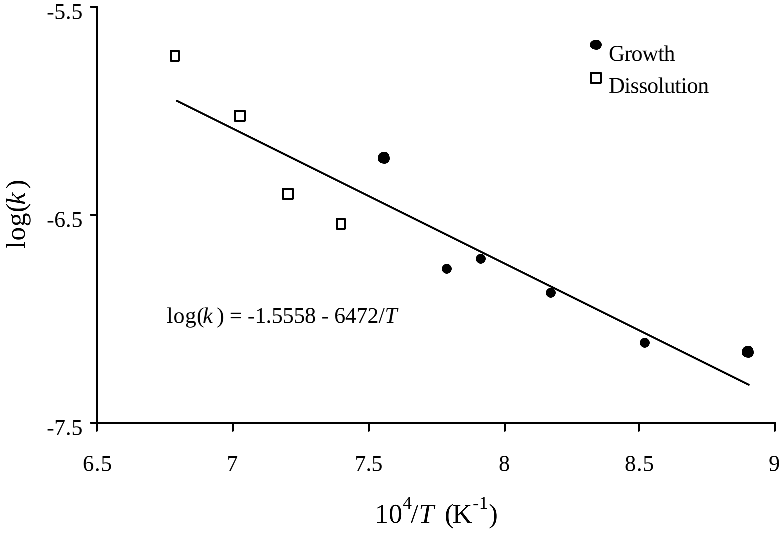

Fig. 3. Mass-Transfer Coefficient for Spinel Crystal Dissolution and Growth as a Function of Inverse Temperature (MS-7 Glass)

To assess the effect of convection on crystal growth and dissolution, we used Equation (4) combined with Levich's formula (17), Equation (5)

$$d = \frac{Dr_S}{kr_G} \qquad \text{(Eq. 4)}$$

$$d = k_L\left(\frac{Dh}{g\Delta r}\right)^{1/3} \qquad \text{(Eq. 5)}$$

where d is the concentration boundary layer thickness, D is the effective diffusion coefficient, r_S is the spinel density, r_G is the melt density, k_L is a constant (= 2.62), h is the viscosity, g is acceleration due to gravity, and Dr is the difference between spinel and melt densities. Figure 4 compares values of d estimated by eliminating D from Equations (4) and (5) with that obtained using Equation (5) with D from Eyring equation

$$D = \frac{k_B T}{l\,h} \qquad \text{(Eq. 6)}$$

where k_B is the Boltzmann constant, T is the temperature, and l is the diameter of the diffusing ion. We used the ionic diameter of O^{2-} for l; smaller ions (Ni^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}) yield larger d values.

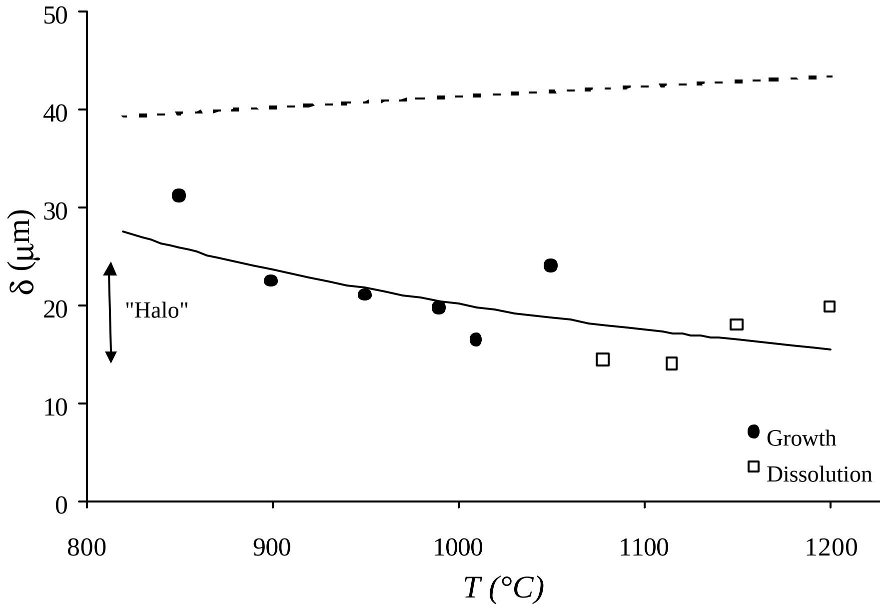

Fig. 4. Different Estimates of the Concentration Boundary Layer Thickness: The vertical double arrow represents the thickness of a "halo" observed around some crystals. The full line is based on Levich's formula, Equation (5), combined with Equation (4). The dashed line is based on the combination of Equations (5) and (6).

A "halo" of clear glass is occasionally observed around spinel crystals (Figure 5). The "halo" thickness, typically 15 to 25 µm, is in good agreement with the calculated values for growth and dissolution (Figure 4). The estimate for d based on Levich-Eyring formula yields a somewhat higher value of 39 to 44 µm. The Eyring equation probably overestimates D. This equation has been derived for self-diffusion coefficients rather than for chemical diffusion that governs crystal growth and dissolution.

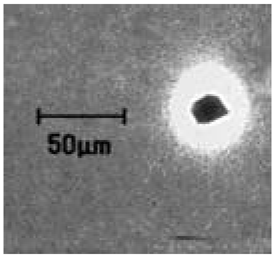

Fig. 5. A "halo" around a spinel crystal (18)

CONCLUSIONS

Reducing the rate of crystal settling would greatly decrease the risk of melter damage owing to the accumulation of solid phase. If the size of spinel crystals that form in the melter is kept small enough, virtually all spinel would be discharged with the glass, while the settling and accumulation of spinel in the melter would be drastically reduced. Consequently, a substantial increase in the waste loading would be achieved by simple inexpensive means. The crystal size is decreased through increasing the crystal number density. Some minor waste components (RuO_2) readily nucleate spinel. An increase in waste loading can be achieved with the current melter technology and within the current schedule. Advanced melters or higher operating temperatures are desirable and may be inevitable in the future. Ultimately, it may become possible, by means of advanced vitrification technology, to drop all processing limits on waste loading, allowing its increase up to its intrinsic maximum level defined by product acceptability (glass durability).

FOOTNOTES

[a] Noble metals (Pd, Rh, and RuO_2) cannot be prevented from settling. Sludges containing both noble metals and other crystalline phases, such as spinel, have not been investigated.
[b] MS-7 glass with 30.2 mass% waste loading and liquidus temperature 1078°C contains 1 mass% spinel at 1048°C in equilibrium. To meet the 1050°C liquidus temperature constraint with the same frit, the waste loading would decrease to 29.2 mass%. At a waste loading of 27.6 mass%, liquidus temperature drops to a conservative level of 1000°C.

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