

BALANCING COST AND RISK BY OPTIMIZING THE HIGH-LEVEL WASTE AND LOW-ACTIVITY WASTE VITRIFICATION

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ABSTRACT

In the currently used melter, the waste loading for nearly all high-level waste (HLW) is limited by crystallization. Above a certain level of waste loading, precipitation, settling, and accumulation of crystalline phases can cause severe processing problems and shorten the melter lifetime. To decrease the cost without putting the vitrification process at an unreasonable risk, several options, such as developing melters that operate above the liquidus temperature of glass, can be considered. Alternatively, if the melter is stirred, either mechanically, by bubbling, or by temperature gradients in induction heating, the melt can contain a substantial fraction of a crystalline phase that would not settle because it would be removed from the melter with glass. In addition, an induction melter can be nearly completely drained. For current melters that operate at a fixed temperature of 1150°C, optimized glass formulation within currently accepted constraints has been developed. This approach is based on mathematically formulated relationships between glass properties and glass composition. Finally, re-evaluating the liquidus-temperature constraint, which may be unnecessarily restrictive for some HLWs, has recently been investigated. An attempt is being made to assess the rate of settling of crystalline phases in the melter and evaluate the risk for melter operation. Based on a reliable estimate of such a risk, waste loading could be increased, and a substantial saving can accrue. For low-activity waste (LAW), the waste loading in glass is limited either by the product quality or by segregation of sulfate during melting. The formulation of constraints on LAW glass in terms of relevant properties has not been completed, and no property-composition relationships have been established so far for this type of waste glass.

INTRODUCTION

The benefit of achieving a high waste loading (W) is a low waste-glass volume, which translates into a shorter cleanup time, a smaller processing facility, and less repository space. Accordingly, the cost of vitrifying high-level waste (HLW) and low-activity waste (LAW) decreases as W increases [1,2]. It can be estimated that each 1 mass% increase in W of Hanford HLW saves the U.S. Department of Energy (DOE) \$670M [3].

For nearly all HLWs, W is limited by the liquidus temperature (T_L) of the glass. If T_L is higher than the lowest temperature (T) of glass in the melter, solid phases are likely to form and accumulate within the melter. Thus, above a certain level of W , precipitation, settling, and accumulation of crystalline phases may cause processing problems and shorten the melter lifetime. To reduce the risk of melter failure, it has been required for HLW glass that $T_L < T$ (T is estimated as 1050°C for melters operating at 1150°C). Considering various uncertainties, HLW glass is often formulated with $T_L < 1000^\circ\text{C}$ or even $< 950^\circ\text{C}$ [4]. Thus low risk is given preference at the expense of high cost.

However, a potential exists for decreasing the cost without unreasonable risk. Several options can be considered:

1. Design melters that do not require the T_L constraint.
2. Develop an approach to glass formulation that maximizes W for the currently accepted T_L constraint.
3. Re-evaluate the T_L constraint and specify a new constraint that would allow higher W without increasing the risk of melter failure.

4. Change the composition of waste so that T_L no longer limits W .
The first three options are discussed in following sections.

ADVANCED MELTER TECHNOLOGY

Consider HLW glass with W limited solely by the product quality. Moreover, let the acceptability of the waste product be defined by a single property, Q , and let this property be a linear function of the waste product composition, i.e.,

$$Q = \sum_{i=1}^N Q_i g_i \quad (1)$$

where g_i is the i -th component fraction in the waste form, Q_i is the i -th partial specific property, and N is the number of glass components. For example the normalized release of boron measured by the product consistency tests [5] has been used for HLW glass acceptability for repository [6].

Generally, the waste form consists of waste and additive mix. Enough additives are used to ensure that

$$Q > Q_C \quad (2)$$

where Q_C is the critical value of Q for product acceptability.

We can write the mass balance for each component as [7]

$$g_i = W w_i + (1 - W) a_i \quad (3)$$

where w_i and a_i are the i -th component fractions in the waste and in the additive mix, respectively. The following equalities are automatically satisfied:

$$\sum_{i=1}^N g_i = 1 \quad \sum_{i=1}^N w_i = 1 \quad \sum_{i=1}^N a_i = 1 \quad (4)$$

Here N is the same in each sum, thus allowing the component fraction to be zero if it is absent in the additive mix. By Equations (1) and (3), Equation (1) can be rewritten in the form

$$Q = W Q_W + (1 - W) Q_A \quad (5)$$

where

$$Q_W = \sum_{i=1}^N Q_i w_i \quad Q_A = \sum_{i=1}^N Q_i a_i \quad (6)$$

By (2) and (5), the waste form is acceptable if

$$W \leq 1 - \frac{\Delta Q}{Q_A - Q_W} < 1 \quad (7)$$

where $\Delta Q = Q_C - Q_W$. It follows from (7) that for given Q_C and Q_W , the maximum W can be achieved if Q_A is as large as possible. By Equation (6), the highest value of Q_A equals to the highest Q_i among the N

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components. Thus the best result is achieved when only one component (that with the highest Q_i) is added to the waste in a minimum amount sufficient to obtain a satisfactory product.

This conclusion is based on the assumption that the linear Equation (1) adequately describes the real behavior. Indeed, it has been shown that W of some HLWs at Hanford can be maximized with the minimum necessary addition of silica [8,9]. However, Equation (1) is not valid for wastes with high sodium content, such as some HLWs and all LAWs at Hanford. These wastes require a balanced mix of several components for the best result. Hence, product quality can be specified using any number of properties that are nonlinear functions of composition.

But even in this general case, a maximum W exists that meets the realistic quality constraints. Taking just one step further, consider two property requirements, such as $Q > Q_C$ and $P > P_C$, where P and P_C are the additional property and its critical value. If both Q and P depend linearly on composition, we can write Inequality (7) also for P . Waste loading is then limited by Q if $\Delta Q/(Q_A - Q_W) > \Delta P/(P_A - P_W)$ and vice versa.

For a waste glass with W limited solely by product quality, processing technology should be developed to ensure that the product could be made on a cost-effective basis. If such a technology appears too risky or too costly, and compromising the product quality is out of the question, W must be decreased to meet the constraints imposed by processing. Then P is a processing-related property that dictates the waste loading.

Current Joule-heated melters with Inconel electrodes allow little flexibility for variability in glass properties [10]. Melt viscosity is required to be between 2 and 10 Pa·s at 1150°C. Melt electrical conductivity is required to be within 10 and 100 S/m at 1150°C, and melt T_L is required to be lower than 1050°C. Also, the melt is required to be single-phase (phase segregation is not permissible). The loading of a majority of HLWs is limited by the T_L constraint. For LAW, product quality limits W in most cases, except when the waste has a high concentration of sulfate. Then the single-phase constraint will be limiting as in the case also for borosilicate glasses containing high concentrations of phosphate.

Several options exist for developing melters that do not require a T_L constraint:

1. In high-temperature melters, T_L does not limit W if the melter is operated at a T that is sufficiently higher than T_L [11,12] ($T > T_L + 100^\circ\text{C}$ is a generally accepted level).
2. In a stirred melter, either mechanically [12-14], by bubbling [12,15-17], or by temperature gradients (as in induction heating [17-19]), the melt can contain a substantial fraction of a crystalline phase that does not settle because it is removed from the melter with glass. In addition, an induction melter can be nearly completely drained.
3. In bottom-drained melters with steep sloping walls, removing the settled sludge from the melter allows processing glass with a higher T_L without a substantial change in the current melter design [17].

Current programs use ceramic Joule-heated melters with Inconel electrodes that have been tested for decades and are considered reliable and demonstrated. A new technology would require some time to get established and accepted. Even though future savings will many times offset the cost of melter development, the budget restrictions do not allow funding of new technology development within any given fiscal year. Thus, the advanced melter technology option seems unlikely at present. Considering that HLW vitrification at Hanford will require decades to complete, the question of advanced melting technology will certainly reappear in the future.

OPTIMIZED GLASS FORMULATION

The second option, optimizing glass formulation within currently accepted constraints, has been developed at PNNL [7] and widely applied. This approach is based on mathematically formulated relationships between glass properties and glass composition. These relationships often have a form of Equation (1) or a second-order polynomial with a limited number of squared and crossproduct terms [10, 19, 20]. The partial specific properties in Equation (1) are obtained by fitting Equation (1) or its extended second-order version to extensive databases being developed from systematic measurements based on statistically designed test matrices. These databases cover HLW glass composition regions applicable to Hanford [10], Savannah River [21], Idaho [22], and other HLWs [23,24]. Special attention is being paid to T_L as the major W -limiting property.

Substituting for g_i from Equation (3) into Equation (1) for each constrained property, we get a series of relationships between glass properties, W , and a_i s for given waste compositions. Using these relationships, glass composition is optimized [10,25]. Thus, for any waste composition, it is possible to find a glass composition that would meet all constraints while maximizing the waste loading. This approach has been applied to estimating the effectiveness of pretreatment and blending options for Hanford and Idaho wastes and for assessing the amount of glass to immobilize HLW at Hanford [26] and Los Alamos National Laboratory [27].

CRYSTALLINITY CONSTRAINT

The third option, re-evaluating the T_L constraint, has been recently investigated [28]. A small accumulation of solid phase does not jeopardize melter performance. The fraction of crystals in melt at $T < T_L$ varies from negligible to high. Thus, the T_L constraint may be unnecessarily restrictive for glasses that precipitate tiny fractions of crystalline phase below T_L .

To determine the maximum acceptable fraction of crystalline phase in glass, it is necessary to assess the rate of settling of crystals in the melter and to evaluate the risk for melter operation. The settling rate depends on the crystal fraction and size, and the temperature and velocity distribution within the melter. Based on this assessment of the impact of crystalline phase on melter performance, W can be increased. Furthermore, sensible limits for problem constituents (such as Cr) in the melter feed can be estimated more accurately, blending requirements can be reduced, and cost and risk for different pretreatment and blending options can be compared.

The most common crystalline phases that precipitate from HLW glasses at $T > 1050^\circ\text{C}$ are spinel (a solid solution of NiFe_2O_4 with other spinel-forming oxides, including Cr_2O_3 and MnO) and Zr-containing phases [29-33]. Spinel forms in glasses produced at West Valley [34] and Savannah River [35] and in HLW glasses formulated for Hanford [10,29]. The effect of the concentration of spinel-forming components in glass on the equilibrium fraction of spinel is shown in Figure 1.

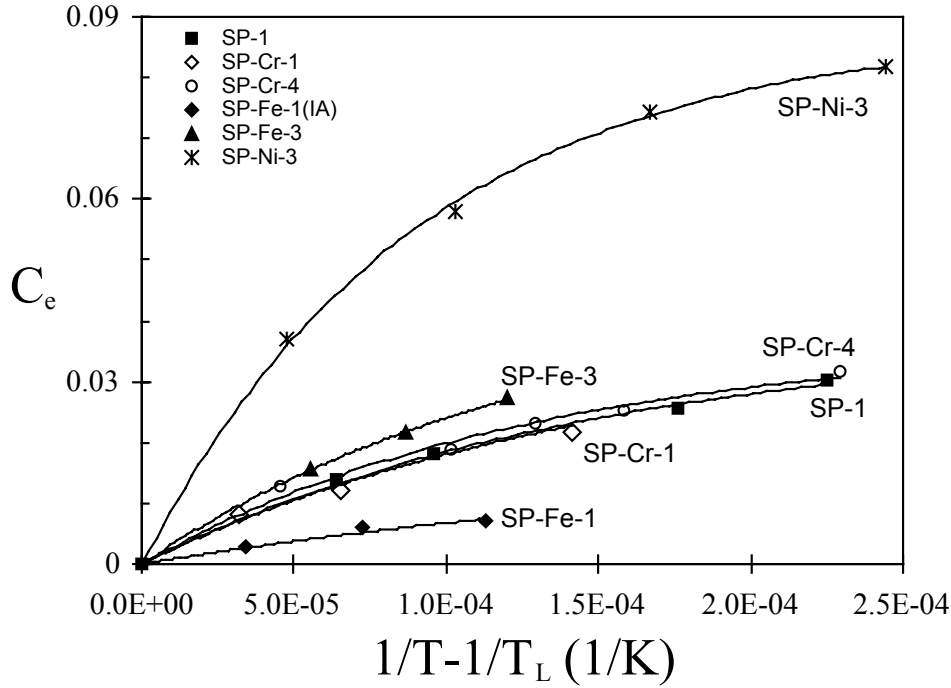


Figure 1. Equilibrium Fraction of Spinel in Glasses with Varied Spinel-Forming Components as a Function of $\theta = 1/T - 1/T_L$ [36] (spinel-forming oxides, in mass%, are Cr_2O_3 0.22, NiO 0.52, and Fe_2O_3 12.50 in SP1; Cr_2O_3 0.00 in SP-Cr-1 and 1.20 in SP-Cr-4; NiO 3.00 in SP-Cr-3; Fe_2O_3 6.00 in SP-Fe-1 and 15.00 in SP-Fe-3)

As Figure 1 shows, the spinel fraction in SP-Fe-1 glass is < 1 mass% even at temperatures far below T_L , whereas for SP-Ni-3 glass, the spinel content increases sharply with decreasing T . Suppose a melter can tolerate 1 mass% spinel in glass at 1050°C. With this constraint, W can significantly increase for low-Fe waste, but would be only slightly higher for Ni-rich waste.

The spinel equilibrium fraction (C_o) depends on T as [37]

$$C_o = C_{\max} \left\{ 1 - \exp \left[-B_L \left(\frac{1}{T} - \frac{1}{T_L} \right) \right] \right\} \quad (8)$$

where C_{\max} , and B_L are composition-dependent coefficients. These coefficients and T_L can be expressed as functions of glass composition using Equation (1).

The difference between T_L and the temperature at which $C_o = C_{acc} \ll 1$ is

$$\Delta T = \frac{T_L^2}{C_{\max} B_L} C_{acc} \quad (9)$$

where C_{acc} is the acceptable fraction of crystallinity. For $C_{acc} = 0.01$, ΔT is between 20 and 120°C.

Spinel in HLW glass is a solid solution of nichromite (NiCr_2O_4), trevorite (NiFe_2O_4), and magnetite (Fe_3O_4). Because of the magnetite component, spinel formation is sensitive to glass redox. Ferrous-ferric ratio in glass depends on the oxygen partial pressure (p_{O_2}) and temperature:

$$\log \frac{Fe[II]}{Fe[III]} = -\frac{1}{4} \log(pO_2) + \frac{\Delta H_r}{2.303RT} + \frac{1}{2} \log(a_{O^{2-}}) + C' \quad (10)$$

where $a_{O^{2-}}$ is the oxygen ion activity coefficient, $\Delta H = -115$ kJ/mol and $(1/2)\log(a_{O^{2-}}) + C' = 3.78$. Assuming that iron in molten glass is at equilibrium with oxygen bubbles (101 kPa), oxygen is released into bubbles as the melt temperature increases. Gas release may have a significant impact on the melt flow and heat transfer in the melter. The iron redox change impacts spinel equilibrium.

Liquidus temperature for spinel phase is a function of p_{O_2} . At $p_{O_2} > 1$ Pa, T_L decreases as p_{O_2} increases. At $10^{-6} < p_{O_2}$ (Pa) < 1 , T_L is virtually independent of p_{O_2} , and at $p_{O_2} < 10^{-6}$ Pa, T_L decreases with decreasing p_{O_2} due to the precipitation of metallic iron. Figure 2 shows the effect of ferrous-ferric ratio on the T_L .

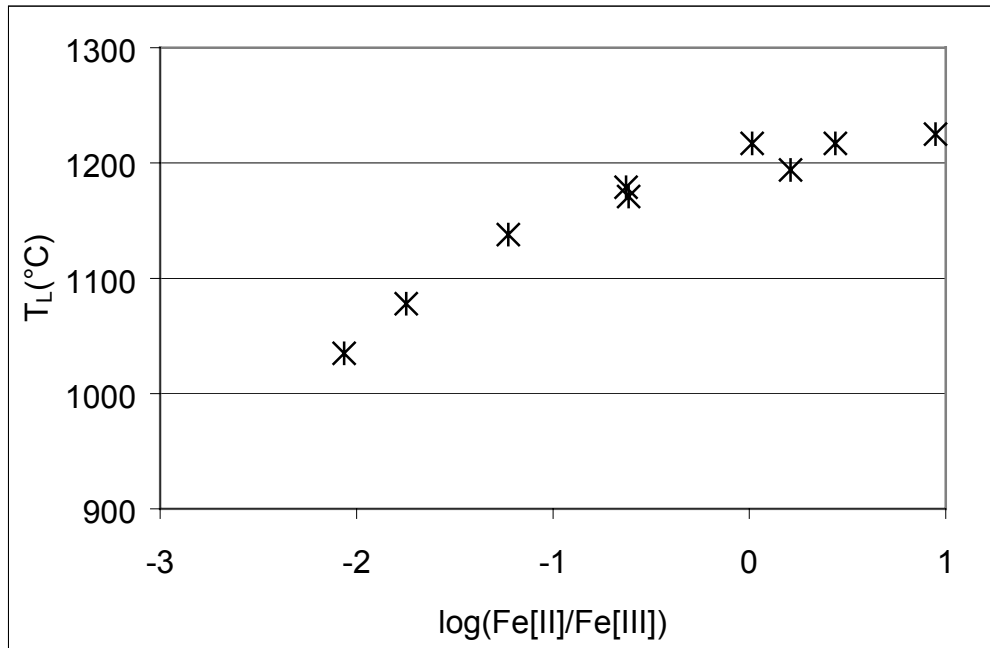


Figure 2. Liquidus temperature versus log(Fe[II]/Fe[III])

Crystallization kinetics determines the rate at which equilibrium is reached. For spinel, the evolution of crystallinity is described by the Kolmogorov-Mehl-Avrami-Johnson equation [37]:

$$C = C_e \left\{ 1 - \exp[-(kt)^n] \right\} \quad (11)$$

where C is the spinel fraction in molten glass, n the Avrami exponent ($n = 1.5$ for spinel) [37] and

$$k = k_0(n_s) \exp\left(-\frac{B_k}{T}\right) \quad (12)$$

is the crystallization rate coefficient; k_0 , and B_k are composition-dependent coefficients. In addition, k_0 is a function of the crystal number density, n_s , which depends on the presence of nucleation sites provided by minor waste components such as RuO_2 , Ag_2O , or Cu_2O [38].

Minor components have little effect on spinel equilibrium, but have a profound impact on spinel crystallization kinetics. This is because minor components provide heterogeneous nuclei for spinel crystallization. An addition of RuO₂ increases by approximately 3.2 times from the baseline glass. Addition of Ag that precipitates Ag-Cu colloid increases the number density of spinel crystals nearly 500 times [38]. Glass temperature history also affects n_s [39], which is higher in the glass heated from room temperature than in the glass cooled from $T > T_L$.

If T changes during crystallization, the crystallization rate is represented by the differential equation [40]

$$\frac{dC}{dt} = nk(C_e - C) \left[-\ln \left(1 - \frac{C}{C_e} \right) \right]^{(n-1)/n} \quad (13)$$

Equation (11) is a solution of Equation (13) for $T = \text{constant}$.

Spinel is one of the intermediate crystalline compounds that form during the batch melting reactions (Figure 3). Melting reactions in HLW glass batches were investigated by Anderson et al. [41], Smith et al. [42], and Vienna et al. [43]. The initial melting reactions were studied by Izak et al. [44]. The main HLW feed melting reaction is that between nitrates and silica at 650 to 750°C. Spinel precipitates from the nitrate melt and later dissolves in the glass-forming melt. This spinel does not contain Cr because Cr(VI) is the dominant valency in molten nitrates. This Cr-free spinel dissolves in the glassforming melt. In molten glass, crystals grow at $T < T_L$ if $C < C_o$ and dissolve when $C > C_o$ or $T > T_L$. As the crystals circulate with molten glass within the melter pool, they undergo changes in each cycle.

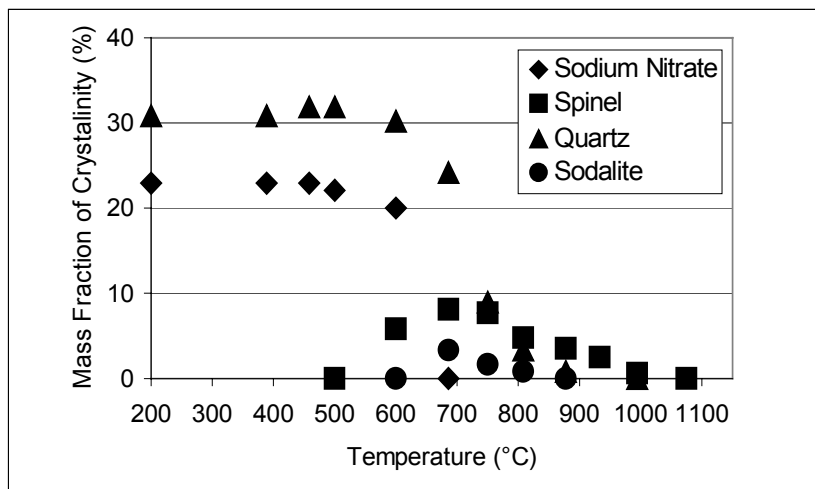


Figure 3. Mass fractions of crystals in MS-7 feed versus temperature at 4°C/min

Spinel particles affect each other during settling in molten glass. In a laboratory crucible, spinel settling usually drives a single flow-cell [45]. The settling depth in the cell axis increases in accordance with the Stokes law if the initial period of crystal growth is considered [46].

A HLW glass melter was modeled using the Glass Service GS-CAD model code [47] is shown in Figure 4. The melter geometry was set up using PNNL blueprints [48]. The slurry-fed ceramic melter (SFCM), designed and operated at Pacific Northwest National Laboratory (PNNL) [48], was selected for the modeling work. The melt is Joule-heated by single-phase electric current from three submerged bock electrodes [49]. Measured MS-7-glass properties were used when available; other melt properties were

taken from the literature [50-52]. The temperature and flow in both cuts (cross and longitudinal) show the good mixing ability of this type of melter.

The operation parameters and boundary conditions were set up according to published values [50,51,53]. The glass pull was 1080 kg/day. The surface temperature was 900°C for glass, 100°C for slurry, and 500°C for the cold cap. The melter operating temperature was 1150°C. The temperature and flow in both cuts (cross and longitudinal) show the good mixing ability of this type of melter.

Glass temperature history is rather wild. Glass circulates many times before it is discharged. Its temperature decreases and increases in each cycle, though the difference between maxima and minima are small (approximately 30°C with occasionally up to 70°C). Spinel crystals are subjected to similar conditions.

A spinel settling model is being developed [55]. The rheology of spinel sludge was studied by Mika et al. [56]. Spinel sludge behaves as a pseudoplastic rheopectic liquid.

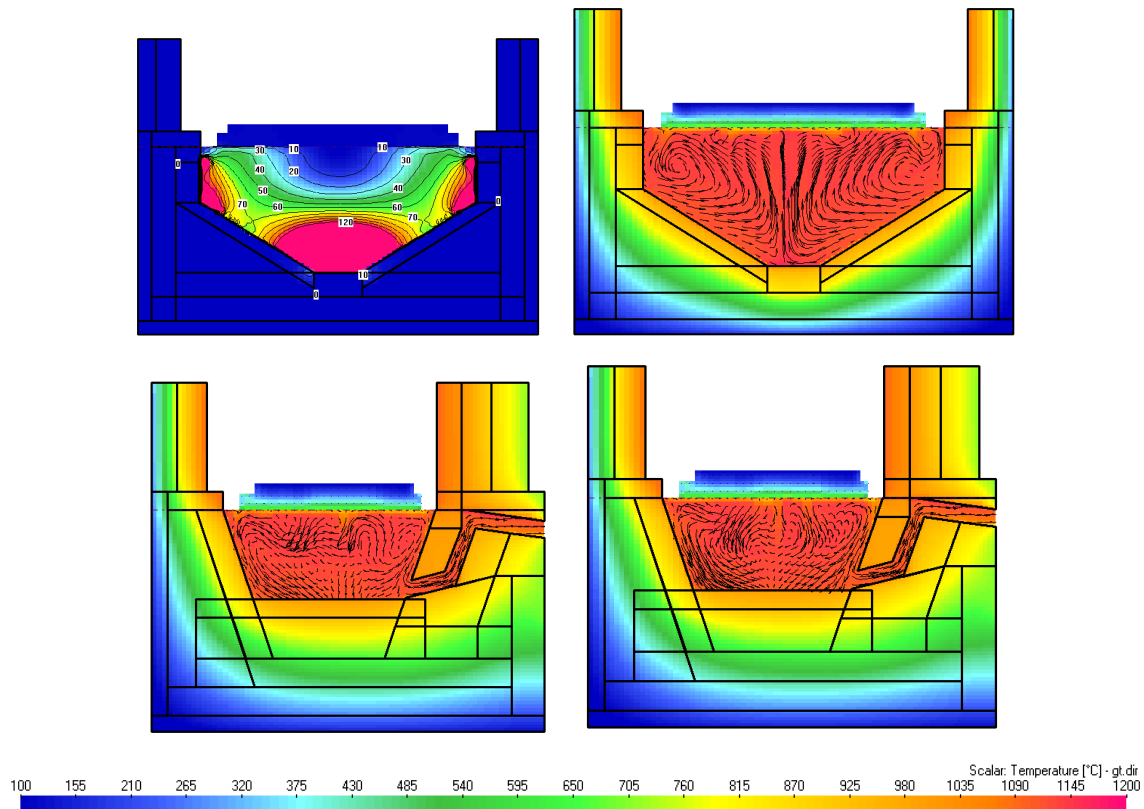


Figure 4. Examples of Electric (in kW/m³), Temperature, and Flow Fields [54]

CONCLUSIONS

Three methods exist for balancing the cost and risk of HLW and LAW vitrification: processing the glass in advanced melters, optimizing glass formulation within the current set of constraints, and establishing new constraints that are based on deeper knowledge of melter performance. Advanced melters are being developed, but may take some time before being accepted by end users. Optimized glass formulation has been developed, but is being consistently applied only for formulation of INEEL glass. For establishing

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new processing constraints, data are generated on the kinetics of spinel crystallization and dissolution, and on the spinel settling mode and rate in molten glass. These data are used to develop physical and mathematical models that predict the rate of spinel settling in the melter and are tools for designing and operating melters that process glasses with high waste loading at low operation risk. For LAW glasses, predictive tools relating glass composition to long-term performance are being developed.

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