The effect of high-level waste glass composition on spinel liquidus temperature

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

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Date Published
November 2012

To be Presented at
10th International Symposium on Crystallization in Glasses and Liquids

Clausthal University of Technology
Goslar, Germany

09/23/2012

Published in
Journal of Non-Crystalline Solids

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The effect of high-level waste glass composition on spinel liquidus temperature

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Abstract

Spinel crystals precipitate in high-level waste glasses containing Fe, Cr, Ni, Mn, Zn, and Ru. The liquidus temperature (T_L) of spinel as the primary crystallization phase is a function of glass composition, and the spinel solubility (c_0) is a function of both glass composition and temperature (T). Previously reported models of T_L as a function of composition are based on T_L measured directly, which requires laborious experimental procedures. Viewing the curve of c_0 versus T as the liquidus line allows a significant broadening of the composition region for model fitting. This paper estimates T_L as a function of composition based on c_0 data obtained with the X-ray diffraction technique.

Key words: waste glass; spinel; liquidus temperature;

1. Introduction

High-level nuclear waste (HLW^{**}) contains 40 to 60 chemical elements. Borosilicate glass is a chemically durable waste form capable of dissolving HLW oxides and halides and keeping them immobilized as long as the radioactive components do not decay. Because of the large number of

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**High-level waste is the highly radioactive waste material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations; and other highly radioactive material that is determined, consistent with existing law, to require permanent isolation.

components and a large compositional variability, where several hundreds of batches of different composition are anticipated for Hanford (Washington, USA) alone, mathematical models are indispensable for relating key properties to HLW glass composition such as viscosity, electrical conductivity, and chemical durability. The liquidus temperature (T_L) of the primary crystalline phase is one of such properties, and upon vitrification spinel is the primary crystalline phase of most U.S. wastes from Pu production. Spinel crystals easily form during waste glass melting and exist in the melt at relatively high temperatures, at which they can interfere with melter operation [[1]-[24]]. Several studies were performed to obtain the liquidus temperature (T_L) of spinel as a function of glass composition [[1],[2],[4],[8],[10],[12],[22]].

The experimental determination of T_L is based on the identification of the highest temperature at which spinel can exist in glass at equilibrium. Spinel crystals are detected in quenched melts optically or with X-ray diffraction (XRD) [[18],[25][26]]. Both techniques require multiple melts and laborious sample preparation. Moreover, measuring T_L poses numerous experimental difficulties including the control of redox reactions, glass homogeneity, and sample volatility [[4]]. The method based on differential scanning calorimetry is ruled out by the very low fraction of spinel precipitated (several mass%) and the low thermal effect of the diffusion-controlled process of spinel crystallization.

In contrast with the time-consuming and laborious direct methods for measuring T_L , the experimental determination of the spinel solubility (c_θ) is relatively easy. Determining c_θ as a function of glass composition and temperature only requires quantitative XRD on specimens heat treated at various temperatures below T_L that are doped with a known standard. While the direct method determines T_L via extrapolation of the c_θ versus temperature (T) function to $c_\theta = 0$, this study estimates the T_L of glasses from each $c_\theta(T)$ data point. It is based on the simple idea that the temperature at which the c_θ was obtained is the liquidus temperature of the matrix glass [[27]]. Since the matrix glass composition changes as spinel precipitates, the composition region for model fitting significantly broadens without

the necessity of making the corresponding glasses and the separate laborious determination of T_L for each. Moreover, having a c_0 data set per glass provides an opportunity to detect sample alterations caused by volatility, redox, and/or crystallization upon cooling. These effects are not easily observed when a single value is determined by optical measurements.

Although the idea of using c_0 data for T_L determination appears simple, it faces its own challenge when applied to spinel. Spinel that precipitates in HLW glasses are solid solutions in the form $A^{2+}B^{3+}_2O_4$, containing Cr^{3+} , $Fe^{2+/3+}$, Ni^{2+} , $Mn^{2+/3+}$, and Zn^{2+} plus minor components, such as Al^{3+} , Ru^{4+} , and Rh^{3+} . Oxides of these elements can be combined to make various spinel types. Thus, oxides of Fe, Cr, and Ni can be combined into four spinel end members: trevorite ($NiFe_2O_4$), nichromite ($NiCr_2O_4$), chromite ($FeCr_2O_4$), and magnetite (Fe_3O_4) with complete solid solutions existing between all. Various reports show that spinel composition changes with both glass composition and temperature [[4],[28],[29]] and may not be uniform within the crystals because of changes in melt composition and redox [[12]]. The authors are not aware of any systematic study relating spinel composition to the conditions of crystal formation.

Because the composition of the matrix glass at equilibrium with spinel depends on spinel composition, the lack of precise knowledge of spinel composition complicates our task of obtaining T_L as a function of glass composition. We circumvent this obstacle by either (1) assuming that spinel composition does not change with experimental variables (this approximation is good for small composition regions) or (2) by constructing simple rules for estimating spinel composition based on the content of spinel oxides in glass.

Several studies investigated spinel solubility in HLW glasses [[5],[9],[22],[30]-[33]]. Here we use two data sets, one by Schweiger et al. [[22]] and the other by Matyas et al. [[33]]. In both studies, glass samples were heat treated at various temperatures until the phase equilibrium was established. The mass fraction of spinel in the samples was measured with XRD. Both studies increased the precision of c_0 values with advanced XRD equipment and analysis software.

2. Theory

At phase equilibrium between the melt and the primary crystalline phase, the crystals are surrounded with the matrix glass of a uniform composition. The content and composition of both the matrix glass and the crystalline phase are related to the composition of the original glass (before the crystals were formed) via the i -th component mass balance equation, also known as the lever rule:

$$g_i^0 = (1 - c_0)g_i + c_0s_i \quad (1)$$

where g_i is the i -th component mass fraction in the matrix glass at equilibrium with spinel, g_i^0 is the i -th component mass fraction in the original glass with no spinel, c_0 is the equilibrium mass fraction of spinel phase in the mixture (of spinel and matrix glass), and s_i is the i -th component mass fraction in spinel.

The glass composition region in the composition space has as many dimensions as the number of components that are considered influential. Because the fractions of all components sum to 1, the large number of “crowded” components results in relatively narrow ranges of individual components. This situation favors approximating property-composition relationship with simple functions, such as first- or second-order polynomials. Hence, in spite of the general complexity of phase diagrams, the liquidus hypersurface for spinel is nearly flat within the composition region of HLW glasses [[4],[19]]. This “simplicity of complexity” allows us to postulate the relationship

$$T_L^0 = \sum_{i=1}^N T_i g_i^0 \quad (2)$$

where T_L^0 is the liquidus temperature and T_i is the i -th component liquidus temperature coefficient.

Similar relationships have been applied to the liquidus for sufficiently small composition regions of waste glasses and commercial glasses with various primary crystalline phases [[35]--[36]].

When the glass is allowed to reach phase equilibrium at $T < T_L$ and spinel is the only crystalline phase present in the melt, the temperature becomes a liquidus temperature for the matrix glass from which the spinel precipitated. This follows from the definition of T_L as the maximum temperature at which the glass is at equilibrium with the primary crystalline phase. Suppose we remove spinel from the matrix melt, for example, by allowing it to settle, thus separating it from the matrix glass. From the spinel-free matrix melt, we can precipitate more spinel by decreasing the temperature. This spinel will dissolve completely by returning to the original heat-treatment temperature. Consequently, the T_L of the matrix glass will be given by the formula

$$T_L = \sum_{i=1}^N T_i g_i \quad (3)$$

with the same component coefficients as in Eq. (1) and T_L being identical to the heat-treatment temperature. Substituting for g_i from Eq. (1) into (3), we obtain

$$T_L = \frac{\sum_{i=1}^N T_i g_i^0 - c_0 \sum_{i=1}^N T_i s_i}{1 - c_0} \quad (4)$$

Provided that both c_0 versus T data and the spinel composition data are available, the T_i values can be computed by fitting Eq. (4) to these data. The needed c_0 versus T data can be obtained with XRD.

Crystal composition is obtainable with scanning electron microscopy and energy dispersive spectroscopy

(SEM-EDS) or by chemical analysis if clean crystals isolated from the glass phase that can be dissolved in acid. If the spinel composition data are not available, as is the case in our study, we can still estimate the T_i values by either treating s_i as a set of fitting coefficients or approximating s_i with simple rules specified below (Section 4).

3. Experimental data

The test glasses in the Schweiger et al. study [[22]] were designed as one-component-at-a-time variations of a baseline glass, whose composition is in Table 1. The components marked bold in the table were varied while all other components were kept at the same proportions as in the baseline glass. The composition variations for glasses with spinel primary phase are shown in Table 2. The measured c_0 values for the test glasses heated at a various temperatures, too numerous to be reproduced in this paper, are listed in [[22]]. For illustration, Fig. 1 displays the spread of c_0 values as plotted against the undercooling below the optically determined T_L . Fig. 2 shows the ratio of the sum of NiO and Cr_2O_3 fraction in the original glass to the spinel fraction in the heat treated glass, i.e., $(g_n^0 + g_c^0)/c_0$, as a function of $T_L^0 - T$.

In a separate study, Matyas et al. [[33]] prepared eight simulated nuclear waste glasses. Each of the test glasses presented a compositional variation from a baseline glass containing 28 components. The varied components were Al_2O_3 , Cr_2O_3 , Fe_2O_3 , Li_2O , NiO, and RuO_2 . The remaining 22 components were kept in the same proportions as in the baseline glass. Tables 3a and 3b list the compositions of glasses in two alternative ways, one with simple oxides NiO, Cr_2O_3 , and Fe_2O_3 and the other in terms of spinels NiFe_2O_4 , NiCr_2O_4 , and Fe_3O_4 . Note that expressing a part of the Fe_2O_3 content in terms of FeO changes mass fractions of the remaining components. The mass fractions of the remaining components are grouped into one component called “Others,” presented in Table 4. Table 5 lists the c_0 versus T data

(Matyas et al. [[33]] did not obtain c_0 versus T data for the baseline glass but did measure the T_L^0 of glasses by optical method and the results were close to those measured with XRD).

4. Spinel composition

Neither Schweiger et al. [[22]] nor Matyas et al. [[33]] report spinel composition. For simplicity, we considered spinel in glass as composed from three species, Cr_2O_3 , NiO , and Fe_2O_3 , disregarding other possible constituents such as MnO , Mn_2O_3 , ZnO , noble metal oxides, etc. To compensate for the lack of spinel composition data, we first assumed that spinel composition was independent of the glass composition and undercooling.

The attempt to obtain both the T_S and a single spinel composition by fitting Eq. (4) to data worked for the relatively small composition region of glasses tested by Matyas et al. [[33]] but failed for a significantly larger composition region investigated by Schweiger et al. [[22]] (Fig. 3). In the case of Schweiger et al. [[22]] data, least-squares optimization resulted in negative fractions of NiO and Cr_2O_3 in the glass matrix, and when the negative fractions were eliminated by imposing constraints, the correlation was unacceptably poor. Attempts to obtain s_i as a first-order polynomial function of glass composition and temperature by means of least-squares fitting appeared overparameterized. As a possible alternative, we estimated spinel composition by means of simple rules (stated below) that are based on empirical observations and the notion of partition factors.

Both phases, molten glass and spinel, are solutions of oxides. At equilibrium, the i -th component partition factors, defined as

$$f_i = \frac{s_i}{g_i} \quad (5)$$

are functions of mixture composition and temperature. According to Annamalai et al. [[28]], the Cr_2O_3 fraction is 130 to 220 times higher in spinel than in the matrix glass; for NiO, the corresponding values are 10 to 50. For example, if 3 mass% spinel precipitates in a glass containing 1.2 mass% Cr_2O_3 , and assuming that $f_i \approx 200$, the estimated fraction of Cr_2O_3 in the matrix glass is 0.17 mass% and the fraction of Cr_2O_3 in the spinel is 34 mass%.

Combining Eqs. (1) and (5), we obtain for the matrix glass composition the equation

$$g_i = \frac{g_i^0}{1 + (f_i - 1)c_0} \quad (6)$$

We used this equation to estimate the minimum remaining fractions of Cr_2O_3 and NiO in the matrix glass in equilibrium with large fractions of spinel.

The relative values of f_i for Cr_2O_3 and NiO reported by Annamalai et al. [[28]] are in accordance with the observation that the T_i values of major spinel-forming components decrease in the order $\text{Cr}_2\text{O}_3 > \text{NiO} > \text{Fe}_2\text{O}_3$. For example, Vienna et al. [[4]] obtained the following values of T_s in terms of mole fractions of cations [or, equivalently, oxides expressed as $\text{CrO}_{1.5}$, $\text{FeO}_{1.5}$, etc.; note that this way of expressing glass composition changes the mass fraction values, and thus the T_s in Eq. (2)]: $T_{\text{Cr}} = 3.21 \times 10^4$ K, $T_{\text{Ni}} = 1.41 \times 10^4$ K, $T_{\text{Fe}} = 4.01 \times 10^3$ K. Provided that all these three species are present in the glass, one can conjecture that spinel nucleates as nichromite, then continues to grow first as trevorite or chromite and then as magnetite, while blending these elementary spinels into a solid solution.

Based on these observations, one can hypothesize that one of the following four cases will occur:

1. If the maximum f_i of Cr_2O_3 is reached to form nichromite, and NiO is still available in the matrix glass, trevorite forms until either the maximum f_i of NiO is reached, or $c_0 \approx c_N + c_T$, where c_N and c_T are the mass fractions of nichromite and trevorite, respectively.

2. If the maximum f_i of NiO is reached to form nichromite, and Cr_2O_3 is still available in the matrix glass, chromite forms until either the maximum f_i of Cr_2O_3 is reached, or $c_0 \approx c_N + c_C$, where c_C is the mass fraction chromite in spinel.
3. If the maximum f_i of both Cr_2O_3 and NiO is reached, then magnetite forms until $c_0 = c_N + c_T + c_M$, where c_M is the mass fraction of magnetite in spinel. It is assumed that enough Fe_2O_3 is present in the glass to make this possible.
4. If $c_0 \approx c_N$, nearly all spinel is assumed to be of nichromite composition and the fractions of other simple spinels are neglected, i.e., $c_T \approx c_C \approx c_M \approx 0$.

Accordingly, depending on the relative proportions of Cr_2O_3 and NiO in glass, and assuming that a sufficient amount of Fe_2O_3 is present while disregarding any spinel components other than NiO, Cr_2O_3 , and Fe_2O_3 , spinel can be nearly all nichromite ($c_0 \approx c_N$), a solid solution of nichromite and trevorite ($c_0 \approx c_N + c_T$), a solid solution of nichromite and chromite ($c_0 \approx c_N + c_C$), or a solid solution of nichromite, chromite and magnetite ($c_0 = c_N + c_T + c_M$). This scheme presents a simplification because spinel crystals typically contain all three major oxides, i.e., Fe_2O_3 , NiO, and Cr_2O_3 . As Table 6 shows, this oversimplification affects a relatively small number of data (13 out of 129). On the other hand, large portions of data are constrained by the maximum values of the f_i s.

For the fitting, Schweiger et al. [[22]] data were arranged in one of two different ways. For Model 1, the 129 data points with $c_0 > 0$ were joined with 35 data points that had optically determined T_L values; for these data, $c_0 = 0$, and thus, by Eq. (1), $g_i = g_i^0$. Model 2 did not use optically determined T_L s and was based solely on XRD data, i.e., those with $c_0 > 0$. Fitting Eq. (3) to (T, g_i) data, with g_i values, calculated by Eq. (1) as $g_i = (g_i^0 - c_0 s_i)/(1 - c_0)$, we obtained the liquidus temperature coefficients, T_i . The values of s_i were obtained by applying stoichiometry to the c_i estimates ($i \equiv N, C, T, M$, where the subscripts denote nichromite, chromite, trevorite, and magnetite, respectively). Afterwards, g_i and s_i

values for Cr_2O_3 and NiO were determined using Eqs. (5) and (6) for all data where this scheme would result in f_s larger than the maximum admissible values, i.e., 200 and 50 for Cr_2O_3 and NiO , respectively.

5. Results

5.1 Models based on Schweiger et al. [[22]] data

Data for which $|T_L - T| > 60$ K (here T is the test temperature and T_L is the estimated liquidus temperature for the matrix glass) were considered outliers and were not included in model fitting—see the cumulative histogram in Fig. 4. The number of outliers was 11 in Model 1 (out of 164 data points; 2 were optical T_L values) and 9 in Model 2 (out of 129 data points). The outliers could indicate erroneous data, but they also are indicative of curved areas of the liquidus surface away from the region in which Eq. (3) is applicable.

Table 7 lists the T_i values and compares them with the T_s previously published. Not surprisingly, the R^2 is higher for Model 2 (0.967) than for Model 1 (0.948); as expected, R^2 values are lower when data for $c_0 = 0$ and $c_0 > 0$ are treated separately (Fig. 5). However, T_L values estimated with Model 1 and Model 2 differ little (Fig. 6).

The effect of various components on the T_L can be judged by the change of T_L when replacing the SiO_2 with an i -th component. As the T_i coefficients listed in Table 7 for Model 1 and 2 imply, 0.1 mass% of Cr_2O_3 , when added at the expense of SiO_2 , changes T_L by 29-38 K, NiO by ~15 K, Fe_2O_3 by ~2 K, Al_2O_3 by ~2 K, and Li_2O by -4 to -3 K. The maximum content of RuO_2 in the test glasses was 0.087 mass% (Table 1). Adding this amount to a Ru-free glass leads to a T_L increase of ~14 K.

5.2 Models based on Matyas et al. [[33]] data

Whereas the large composition region used by Schweiger et al. [[22]] did not allow a reasonable fit while assuming a constant spinel composition, this approximation worked for the smaller composition

region investigated by Matyas et al. [[33]] (Fig. 3). We fitted Equation (4) to data listed in Tables 3 and 5 by optimizing, with least squares optimization, the values of T_i and the $s_i T_i$ product. Two data points were not used for calculation: Ni1.5/Al10 and Ni1.5/Fe17.5, both at 850°C; see the italicized numbers in Table 5.

Table 8 shows T_i and Table 9 (the two right columns) s_i values for two fits, one based on simple oxides (Table 3a) and the other on Ni-Cr-Fe spinels (Table 3b). Judging from the high value of the correlation coefficient, $R^2 = 0.983$, both fits are excellent in spite of the simplifying approximations. Fig. 7 compares the estimated T_L with the temperature at which the glasses were equilibrated. As the right plot in Fig. 7 shows, the way in which the glass composition is expressed does not make a difference for the estimated T_L .

6. Discussion

6.1 Possible biases

As the comparison of T_L estimates (Fig. 5, right, and Fig. 6) indicate, data based on XRD appear biased when plotted against data based on the optical method. In fact, various biases exist:

1. XRD extrapolation bias is caused by two factors:
 - a. Low c_0 values that occur as $T \rightarrow T_L$ are not measured sufficiently accurately by XRD, because of detection limits and a low signal to noise ratio. Thus, low fractions of crystals may be undetected by XRD.
 - b. As $T \rightarrow T_L$, the slope, dc_0/dT , can dramatically increase, leading to overestimated T_L .
2. The optical method can also be biased by various means:
 - a. Crystals can form above T_L because of concentration fluctuation, minor inhomogeneities, melt volatilization, or interaction between the melt and the crucible wall.

- b. Crystals may not be detected below T_L because of the lack of nucleation (unlikely in the case of spinel), because tiny crystals can be missed, or because crystals are present in the bulk but absent in the thin section used for optical microscopy.
- 3. Sample cooling can also lead to misleading results:
 - a. Slow-nucleating and slow-growing crystals can result in a lower value of measured c_0 .
 - b. New crystals may form after the heat treatment during quenching even in melts heat treated at temperatures above T_L .

Our method of obtaining T_L versus composition from c_0 data rests on the assumption that the matrix glass has a uniform composition that is in equilibrium with the crystalline phase, i.e., that concentration gradients are absent in the matrix glass. A presence of concentration gradients would imply that the g_i values in Eq. (1) are average compositions of matrix glasses, bringing an additional uncertainty to the T_L coefficients listed in Tables 7 and 8. The validity of the glass uniformity assumption can be tested by direct measurements or by preparing matrix glass and checking its T_L .

6.2 Spinel composition uncertainty

Table 9 and Fig. 8 summarize estimated spinel compositions for both studies. The fitted composition based on Matyas et al. [[33]] data is mainly a solution of trevorite and magnetite with chromite as a minor component. In terms of mole fractions of basic spinels, the fitted spinel consisted of 46–49 mol% trevorite, 47–49 mol% magnetite, and ~5 mol% nichromite. This can be compared with the composition of spinel crystals that settled in Ni1.5 glass [[37]] and examined with SEM-EDS. In the atomic fractions of cations, that spinel contained 0.614 Fe, 0.348 Ni, 0.022 Cr, and 0.016 Mn; omitting Mn, it is equivalent to 97 mol% trevorite and ~3 mol% chromite.

For the Schweiger et al. [[22]] study, spinel composition varies considerably. Nichromite is the dominant phase followed by trevorite, while chromite and magnetite are minor ingredients, indicating a

bias in favor of chromite. The difference in the temperature ranges between the studies could lead to differences in spinel composition: the range of temperatures in the Matyas et al. [[33]] study (844–1150°C) was narrower and the maximum was shifted to lower temperature than in the Schweiger et al. [[22]] study (844–1431°C). One can speculate that the lower temperature favors the formation of magnetite.

Fortunately, uncertainty in spinel composition estimates did not compromise agreement between measured and estimated T_L . Because values of T_i and s_i occur in Eq. (4) as a sum of $T_i s_i$ products, a compensation effect between these values possibly offsets the uncertainty in s_i estimates.

6.3 Spinel equilibrium fraction

Using the T_i and s_i coefficients, we can estimate c_0 versus T curves for glasses within the composition regions of the test glasses studied. After rewriting Equation (4) as

$$T_L = \frac{T_L^0 - c_0 T_S}{1 - c_0} \quad (5)$$

where T_L^0 is defined by Equation (2) and $T_S = \sum_{i=1}^N T_i s_i$, we obtain for c_0 the expression

$$c_0 = \frac{T_L^0 - T_L}{T_S - T_L} \quad (6)$$

By replacing the T_L symbol with T , the temperature at which the melt was equilibrated, we can recover the original data. Moreover, based on T_i values and the knowledge or a reasonable estimate of

the crystalline phase composition, we can use Eq. (6) to estimate the “solubility limit” of crystal-forming components in glasses within the composition region of the model validity.

Fig. 9 demonstrates good agreement between the calculated curves and Matyas et al. [[33]] data listed in Table 5. Both T_L^0 and T_S values were obtained using T_i and s_i values listed in Tables 8 and 9 (simple oxides). The T_L^0 values are listed in Table 10 and $T_S = 6528^\circ\text{C}$. For small T_L values, Eq. (6) yields the theoretical maximum spinel content in the glass as $c_M = T_L^0 / T_S$, where the temperatures are in K. The c_M values are shown in Table 10. These values are 15 to 32% higher than the sum, c_{max} , of NiFe_2O_4 , NiCr_2O_4 , and Fe_3O_4 mass fractions listed in Table 3b. This indicates that the linear model cannot be extrapolated to temperatures much lower than 850°C , even though the spinel contains some additional components (2–5% of the glass).

6.4 Composition region extension

As has been stated in the Introduction, the composition region of the T_L model validity broadens when c_0 versus T data are used for model fitting. Table 11 compares the composition region of the matrix glasses with the composition region of the original test glasses, showing that the ranges of the spinel forming components substantially increased (NiO by 18%, Cr_2O_3 by 114%, and Fe_2O_3 by 84%).

In comparison with the optical method [[22]], the composition ranges covered by the XRD extrapolation method increased by 1 to 5% and the temperature range of T_L increased from 1021 – 1363°C of optically determined T_L to 843 – 1396°C of Model 1 and 836 – 1493°C of Model 2.

7. Conclusions

A simple component mass balance allows the spinel content (c_θ) versus temperature (T) curve to be viewed as the liquidus line, thus significantly broadening the composition region for model fitting. Using published $c_\theta(T)$, composition coefficients for T_L and spinel composition were estimated by least-squares

optimization. Although the model is based on various simplifying assumptions, it fits data reasonably well.

Acknowledgments

The authors gratefully acknowledge the financial support of the U.S. Department of Energy Federal Project Office Engineering Division for the Hanford Tank Waste Treatment and Immobilization Plant. Pavel Hrma was supported also by the World Class University program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R31-30005). The authors greatly appreciate Albert Kruger for his assistance and guidance. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC05-76RL01830.

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Figure captions

Fig. 1 Spinel mass fraction versus undercooling below optically determined T_L .

Fig. 2. Ratio of $\text{NiO} + \text{Cr}_2\text{O}_3$ mass fractions in glass to c_0 versus undercooling below optically determined T_L ; the trend line is a hyperbola $y = x_0/x$, where $y = (g_n^0 + g_c^0)/c_0$, $x = T_L^0 - T$, and $x_0 = 180$ K.

Fig. 3. Matrix glass component ranges for glasses varying the components shown based on data sets by Schweiger et al. [[22]] and Matyas et al. [[33]]

Fig. 4. Cumulative histogram of deviations between estimated T_L and heat-treatment temperature (Model 1)

Fig. 5. Estimated T_L versus test temperature (left) and optically measured T_L (right)

Fig. 6. Estimated T_L , Model 2 versus Model 1

Figure 7. Estimated T_L versus test temperature (left); comparison of T_L estimates based on alternative ways of expressing glass composition (right)

Fig. 8. Spinel composition based on Schweiger et al. [[22]] data (Model 1) and Matyas et al. [[33]] data

Fig. 9. Measured data and fitted lines for equilibrium spinel mass fraction [33]

Table 1. Baseline glass composition in mass fractions [[22]]

Al₂O₃	0.1000	MgO	0.0015	PdO	0.00009
B₂O₃	0.1000	MnO	0.0200	Rh₂O₃	0.00003
BaO	0.0005	Na₂O	0.1500	RuO₂	0.00018
Bi₂O₃	0.0000	Nd ₂ O ₃	0.0007		
CaO	0.0000	NiO	0.0100		
CdO	0.0014	P₂O₅	0.0125		
Ce ₂ O ₃	0.0005	PbO	0.0037		
Cr₂O₃	0.0050	SiO₂	0.4333		
F	0.0010	SO ₃	0.0030		
Fe₂O₃	0.1000	SrO	0.0024		
K₂O	0.0000	TiO ₂	0.0004		
La ₂ O ₃	0.0007	ZnO	0.0006		
Li₂O	0.0275	ZrO ₂	0.0250		

Table 2. List of test glasses with component varied [[22]]

ID	Oxide	Mass fraction	ID	Oxide	Mass fraction	ID	Oxide	Mass fraction
Al-06	Al ₂ O ₃	0.0600	Cr-02	Cr ₂ O ₃	0.0200	Na-20	Na ₂ O	0.2000
Al-15	Al ₂ O ₃	0.1500	F-02	F	0.0200	Ni-001	NiO	0.0010
Al-20	Al ₂ O ₃	0.2000	Fe-05	Fe ₂ O ₃	0.0500	Ni-02	NiO	0.0200
B-05	B ₂ O ₃	0.0500	Fe-15	Fe ₂ O ₃	0.1500	P-0	P ₂ O ₅	0.0000
B-15	B ₂ O ₃	0.1500	Fe-20	Fe ₂ O ₃	0.2000	P-025	P ₂ O ₅	0.0250
B-20	B ₂ O ₃	0.2000	K-03	K ₂ O	0.0300	Si-30	SiO ₂	0.3000
Bi-025	Bi ₂ O ₃	0.0250	K-06	K ₂ O	0.0600	Si-37	SiO ₂	0.3700
Bi-05	Bi ₂ O ₃	0.0500	Li-015	Li ₂ O	0.0150	Si-50	SiO ₂	0.5000
Ca-035	CaO	0.0350	Li-04	Li ₂ O	0.0400	Zr-001	ZrO ₂	0.0010
Ca-07	CaO	0.0700	Mn-01	MnO	0.0010	Zr-05	ZrO ₂	0.0500
Cr-001	Cr ₂ O ₃	0.0010	Mn-04	MnO	0.0400	NM-0025	NM ^a	0.0024
Cr-012	Cr ₂ O ₃	0.0120	Na-10	Na ₂ O	0.1000			

^aNoble metals: PdO 0.00072, Rh₂O₃ 0.00024, and RuO₂ 0.00144

Table 3a. Glass compositions in mass fractions of simple oxides [[33]]

Glass ID	NiO	Cr ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	Li ₂ O	RuO ₂	Others
Baseline	0.0064	0.0017	0.1451	0.0821	0.0199	0.0000	0.7448
Ni1.29	0.0129	0.0017	0.1441	0.0816	0.0198	0.0000	0.7399
Cr0.3	0.0064	0.0030	0.1448	0.0820	0.0199	0.0000	0.7439
Ni1.5/Al10	0.0150	0.0017	0.1408	0.1000	0.0193	0.0000	0.7232
Ni1.5/Fe17.5	0.0150	0.0016	0.1750	0.0784	0.0190	0.0000	0.7110
Ni1.5/Li3.8	0.0150	0.0017	0.1410	0.0799	0.0380	0.0000	0.7244
Ni1.5/Cr0.3	0.0150	0.0030	0.1436	0.0813	0.0197	0.0000	0.7374
Ni1.5/Ru0.015	0.0150	0.0017	0.1437	0.0814	0.0197	0.00015	0.7384
Ni1.5/Ru0.087	0.0150	0.0017	0.1436	0.0813	0.0197	0.00087	0.7378

Table 3b. Glass compositions in mass fractions of simple oxides and spinels

Glass ID	NiFe ₂ O ₄	NiCr ₂ O ₄	Fe ₃ O ₄	Al ₂ O ₃	Li ₂ O	RuO ₂	Others
Ni1.29	0.0379	0.0025	0.1144	0.0816	0.0198	0.00000	0.7439
Cr0.3	0.0155	0.0045	0.1298	0.0820	0.0199	0.00000	0.7484
Ni1.5/Al10	0.0444	0.0025	0.1068	0.1000	0.0193	0.00000	0.7269
Ni1.5/Fe17.10	0.0446	0.0024	0.1398	0.0784	0.0190	0.00000	0.7158
Ni1.5/Li3.10	0.0444	0.0025	0.1070	0.0799	0.0380	0.00000	0.7281
Ni1.5/Cr0.10	0.0424	0.0045	0.1109	0.0813	0.0197	0.00000	0.7412
Ni1.5/Ru0.015	0.0444	0.0025	0.1096	0.0814	0.0197	0.00015	0.7421
Ni1.5/Ru0.087	0.0444	0.0025	0.1095	0.0813	0.0197	0.00087	0.7416

Table 4. "Others" composition in mass fractions [[33]]

B ₂ O ₃	0.1073	MgO	0.0018
BaO	0.0012	MnO	0.0047
CaO	0.0076	Na ₂ O	0.2505
CdO	0.0087	Nd ₂ O ₃	0.0024
Ce ₂ O ₃	0.0027	P ₂ O ₅	0.0043
Cl	0.0003	SiO ₂	0.5412
CoO	0.0001	SnO ₂	0.0014
CuO	0.0005	SO ₃	0.0011
F	0.0001	TiO ₂	0.0004
K ₂ O	0.0046	ZnO	0.0003
La ₂ O ₃	0.0030	ZrO ₂	0.0558

Table 5. Equilibrium content of spinel phase in glasses in mass fractions [[33]]

T_i , °C	850	875	900	926	950	1000	1008	1025	1050	1070	1080
Ni1.29	0.0268	0.0225	0.0206	0.0151	0.0099	0.0038					
Cr0.3	0.0094	0.0074	0.0045								
Ni1.5/Al10	0.0406	0.0418	0.0379	0.0329	0.0297	0.0253	0.0193	0.0169	0.0071		
Ni1.5/Fe17.5	0.0530	0.0533	0.0484	0.0421	0.0398	0.0347	0.0334	0.0293	0.0260	0.0229	0.0184
Ni1.5Li3.8	0.0328	0.0305	0.0245	0.0208	0.0171	0.0097					
Ni1.5/Cr0.3	0.0331	0.0289	0.0269	0.0211	0.0178	0.0132	0.0072	0.0026			
Ni1.5Ru0.015	0.0347	0.0291	0.0271	0.0206	0.0174						
Ni1.5Ru0.087	0.0339	0.0317	0.0266	0.0224	0.0175	0.0135	0.0108	0.0062	0.0019		

Table 6. Impact of Rules 1 and 2 on Schweiger et al. [[22]] database

Number of glasses with spinel primary phase	35
Number of data	164
Number of data with $c_0 > 0$	129
Number of spinel compositions containing only Cr_2O_3 and NiO	13
Number of spinel compositions with $f_{\text{Cr}_2\text{O}_3} = 200$	112
Number of spinel compositions with $f_{\text{NiO}} = 50$	67

Table 7. Liquidus temperature coefficients (T_i) in °C

	Model 1	Model 2	Schweiger et al. [[22]]		Mika et al.	Hrma et al.		Wilson et al.
			Optical	XRD	[[2]]	[[3]]		[[10]]
Cr_2O_3	29781	39169	26835	30792	27108	19242	21038	20578
NiO	15788	15592	9405	10837	9445	8629	9231	9573
Fe_2O_3	2992	3202	2677	3083	2700	2605	2730	2670
MnO	1790	1442	2875	1336	507	1962	958	
NM ^(a)	20582	21619				31192	15461	
Al_2O_3	2637	2560	2975	3572	2777	3330	2980	2848
B_2O_3	667	616	646	573	346	363	304	
SiO_2	999	754	981	866	1004	838	993	
P_2O_5	1623	1569	2859	1822				
Bi_2O_3	554	150	719	966				
ZrO_2	983	864	1572	1356				
CaO	294	405	-230	37	2215		2162	
MgO					4345	2900	3592	2657
Li_2O	-2983	-2431	-3316	-7027	-1639	-1599	-1587	-1333
Na_2O	-1453	-1461	-1664	-2029	-1565	-1851	-1654	-1756
K_2O	-1037	-839	-1782	-1138	-885		-711	
F	72	-392	1134	1108				
Others	2474	7763	7670	15014				1195
R^2	0.948	0.967	0.957	0.951	0.970	0.940	0.960	0.968

^aNoble metals: PdO, Rh_2O_3 , and RuO_2

Table 8. Liquidus temperature coefficients (T_l) based on simple oxides (Table 3a) and on Ni-Cr-Fe spinels (Table 3b)

	T_l (°C)		T_l (°C)
NiO	15709	NiFe ₂ O ₄	8150
Cr ₂ O ₃	3071	NiCr ₂ O ₄	6301
Fe ₂ O ₃	4723	Fe ₃ O ₄	4882
RuO ₂	16445	RuO ₂	16390
Al ₂ O ₃	4284	Al ₂ O ₃	4274
Li ₂ O	841	Li ₂ O	825
Others	-333	Others	-320
R^2	0.983	R^2	0.983

Table 9. Spinel composition (in mass fractions) based on Schweiger et al. [[22]] data (Model 1) and Matyas et al. [[33]] data (fitted to compositions based on simple oxides [left column] and Ni-Cr-Fe spinels [right column])

	Schweiger et al.			Matyas et al.	
	Max.	Min.	Average	Oxides	Spinel
Cr ₂ O ₃	0.6705	0.0605	0.1783	0.0300	0.0295
Fe ₂ O ₃	0.6582	0.0000	0.4996	0.8011	0.8101
NiO	0.3295	0.0909	0.3221	0.1689	0.1604
NiCr ₂ O ₄	1.0000	0.0000	0.7373	0.0479	0.0447
NiFe ₂ O ₄	0.9098	0.0000	0.2484	0.4843	0.4657
FeCr ₂ O ₄	0.7147	0.0000	0.0108		
Fe ₃ O ₄	0.2905	0.0000	0.0035	0.4678	0.4896

Table 10. Estimated and measured T_L of test glasses and the theoretical maximum spinel content

	$T_L^{0(a)}$	$T_L^{0(b)}$	$T_L^{0(c)}$	C_M	C_{max}
Ni1.29	1008	949	950	0.188	0.155
Cr0.3	914	988	1005	0.175	0.150
Ni1.5/Al10	1109	1074	1075	0.203	0.154
Ni1.5/Fe17.5	1182	1125	1105	0.214	0.187
Ni1.5/Li3.8	1040	1012	1004	0.193	0.154
Ni1.5/Cr0.3	1042	1021	1018	0.193	0.158
Ni1.5/Ru0.015	1041	1051	1087	0.193	0.157
Ni1.5/Ru0.087	1052	1061	1085	0.195	0.156

(a) Based on Table 8 coefficients

(b) Measured via XRD [[33]]

(c) Measured optically [[33]]

Table 11. Composition regions of test glasses and matrix glasses in mass fractions of components for Matyas et al. [[33]] data (model fitted to compositions expressed in simple oxides)

	Minimum		Maximum		Range ^(a)	Increase Ratio ^(b)
	Test glass	Matrix glass	Test glass	Matrix glass		
NiO	0.0064	0.0049	0.0150	0.0147	0.0101	1.18
Cr ₂ O ₃	0.0016	0.0000	0.0030	0.0029	0.0030	2.14
Fe ₂ O ₃	0.1408	0.1120	0.1750	0.1712	0.0630	1.84
Al ₂ O ₃	0.0784	0.0789	0.1000	0.1044	0.0009	1.20
Li ₂ O	0.0190	0.0191	0.0380	0.0393	0.0260	1.07
Others	0.7110	0.7153	0.7448	0.7649	0.0203	1.59

(a) Range covers test glasses plus matrix glasses.

(b) The i -th component Increase Ratio equals the (overall) i -th component range divided by the i -th component range in test glasses.

Fig. 1 Spinel mass fraction versus undercooling below optically determined T_L .

Fig. 2. Ratio of NiO + Cr₂O₃ mass fractions in glass to c_0 versus undercooling below optically determined T_L ; the trend line is a hyperbola $y = x_0/x$, where $y = (g_n^0 + g_c^0)/c_0$, $x = T_L^0 - T$, and $x_0 = 180$ K.

Fig. 3. Matrix glass component ranges for glasses varying the components shown based on data sets by Schweiger et al. [[22]] and Matyas et al. [[33]]

Fig. 4. Cumulative histogram of deviations between estimated T_L and heat-treatment temperature (Model 1)

Fig. 5. Estimated T_L versus test temperature (left) and optically measured T_L (right); R^2 in the legend denoted the correlation coefficient (R^2)

Fig. 6. Estimated T_L , Model 2 versus Model 1

Figure 7. Estimated T_L versus test temperature (left); comparison of T_L estimates based on alternative ways of expressing glass composition (right)

Fig. 8. Spinel composition based on Schweiger et al. [[22]] data (Model 1) and Matyas et al. [[33]] data

Fig. 9. Measured data and fitted lines for equilibrium spinel mass fraction [33]