Thermodynamic Model of Spinel Crystallization in High-Level Waste Glass

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Liquid high-level radioactive waste stored in underground tanks at the Hanford and Savannah River sites represents a serious environmental trouble. The waste can be safely immobilized in alkali-aluminoborosilicate glass. To increase the effectiveness of this technology and thus decrease its cost, the waste loading should be as high as possible. However, the high waste loading brings problems with formation of spinel crystals which can accumulate in a melter and cause pouring difficulties. This risk can be reduced by controlling spinel crystallization. Thus we need to understand the effect of glass-melt composition on spinel crystallization which can be acquired from the proposed model. In the model a solid phase is treated as the solid solution of 4 spinel end-members (trevorite, magnetite, nichromite, and chromite). Molar Gibbs free energy of such solid solution was defined using the simple symmetric regular model with empirical coefficients calculated from the compositions of crystals precipitating at liquidus temperature. For a liquid phase, being a multicomponent oxide mixture, we used the optical basicity concept to estimate the Fe^{2+}/Fe^{3+} ratio and the activity of O^{2-} and calculated end-members activities in the melt. From them we estimated end-members activities in the solid solution using the LeChatelier-Schreder equation and determined the compositions of spinel solid solutions precipitating at liquidus temperature.

INTRODUCTION

Large quantities of liquid high-level radioactive wastes (HLWs), generated in past decades, have been stored in steel underground tanks at the Hanford and Savannah River sites in the United States. The progressive corrosion of the tank's walls can cause the leakage of radioisotopes and thus represents a serious environmental trouble. The only way, how to safely solve this problem, is the conversion of the liquid wastes into a durable solid form. For highly active wastes the best solution is the vitrification technology embedding radioisotopes in a chemically durable alkali-aluminoborosilicate glass. This process already started in 1996 when the first Defense Waste Processing Facility at the Savannah River Site began radioactive operations. The obtained experiences showed that despite of a substantial waste volume reduction, this high temperature procedure is very expensive and its effectiveness significantly depends on the waste loading in glass. The production cost of

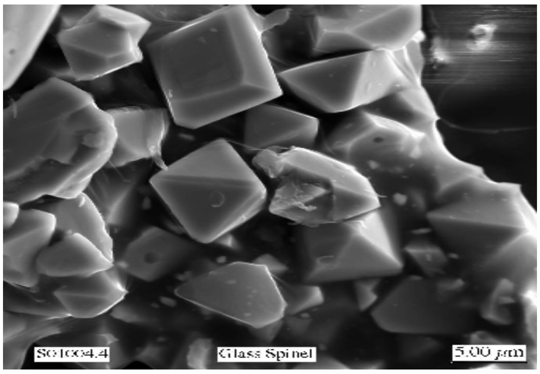

Fig. 1. Spinel Precipitating in HLW Glass.

the HLW glass currently containing 25 wt% of waste was estimated at \$1M per canister. Only at Savannah River it is planned to produce nearly 6,000 canisters of the HLW glass and 1 wt% increase in the HLW glass could reduce cleanup costs by \$200M[1]. During last years a substantial effort has been focused on the increase of the waste loading. This is not an easy task because HLWs are usually rich in Fe_2O_3, NiO, and Cr_2O_3, which form very durable spinel crystals in HLW glassmelts (Fig.1).

The settling and accumulation of spinel crystals, having roughly two times higher density than the melt, in narrow parts of a melter can cause, e.g., pouring difficulties leading to severe problems in operating the melter and can even shorten the melter's lifetime. There have been several approaches how to maximize the waste loading. With currently approved ceramic melters there are two possibilities. The most conservative solution is to avoid precipitation of any spinel crystals. To ensure this, the melt in all parts of the melting tank must be above liquidus temperature (T_{liq}). Because of using Inconel electrodes, HLW melters operate at the nominal temperature of 1150°C and a safety gap is considered to be 100°C; therefore, T_{liq} should not be higher than 1050°C. This constrain severely limits the waste loading because Fe_2O_3, NiO, and above all Cr_2O_3 increase T_{liq} very significantly[2]. Other glass components, of course, also effect T_{liq} thus an optimal glass composition allowing a maximal waste loading could be found. For that, it is necessary to know precisely all effects on T_{liq}. Another approach is based on the assumption that the waste loading can increase to a level at which spinel crystals form if they settle sufficiently slowly to keep spinel deposition below its critical level during the lifetime of the melter. The growth rate of spinel layer in the melter strongly depends on the size and concentration of spinel crystals[3]; therefore, it is important to know how to influence the kinetics of their crystallization. The problems with the spinel sludge could be overcome by using melters with bottom drains (e.g., the cold crucible) enabling the discharge of the accumulated crystals. Even when using this type of a melter, it is important to predict a rheological behavior of the crystals-melt mixture. Plodinec[4] and Mika *et.al.*[5] showed that the mixture behaves as a pseudoplastic rheopectic liquid and its apparent viscosity increases with the concentration of the crystals[6] thus again the prediction of spinel crystallization is important.

To obtain new information on the melt-spinel equilibrium and kinetics of spinel crystallization, we have been developing a thermodynamic model of spinel crystallization that is expanded with the melt optical basicity concept enabling the prediction of Fe^{2+} - Fe^{3+} equilibrium and O^{2-} activity in glassmelts. In this paper we want to demonstrate how this model is able to predict composition of spinel crystals precipitating from a multicomponent aluminosilicate melt.

THEORY

In our approach we have divided the thermodynamic model in two parts; the first part describes the spinel solid phase and the second one a multicomponent glassmelt.

Thermodynamics of Solid Solution

The solid phase precipitating from HLW glass consists of spinel-type crystals containing mainly Cr^{3+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, and O^{2-}, which we consider to be the only components in our spinel crystals[2,7]. We assume that our crystals are a solid solution of four different spinel type crystals called end-members. These spinels are listed in Table. 1.

Table 1. Abbreviations and Numbering of Spinel End-Members

No.	Name	Component	Abbreviation	Formula*
1	Trevorite	S_1	FN	$Fe^{3+}(Ni^{2+}, Fe^{3+})O_4$
2	Magnetite	S_2	FF	$Fe^{3+}(Fe^{2+}, Fe^{3+})O_4$
3	Nichromite	S_3	NC	$Ni^{2+}(Cr^{3+})_2O_4$
4	Chromite	S_4	FC	$Fe^{2+}(Cr^{3+})_2O_4$

* Octahedral positions are in brackets. The priority order of octahedral positions occupation: $Cr^{3+} > Ni^{2+} > Fe^{2+} > Fe^{3+}$.

The solid solution consists of $(n+1)$ components abbreviated as S_1, S_2, …, S_{n+1}. Molar Gibbs free energy of the solid solution, G_m^{ss}, is defined by the simple *symmetric* regular model[8]:

$$G_{\mathrm{m}}^{\mathrm{ss}} = \sum_{i=1}^{n+1} x_i \mu_i^{\circ} + RT \sum_{i=1}^{n+1} x_i \ln x_i + \frac{1}{2} \sum_{i=1}^{n+1} \sum_{j=1}^{n+1} w_{ij} x_i x_j \tag{1}$$

where x_i is the mole fraction of the component S_i in the solid solution, μ_i° is the standard Gibbs free energy of the component S_i, as the standard state a pure crystalline substance was chosen at the pressure and temperature of the system, R is the gas constant, T is the thermodynamic temperature, $n=3$ (in our case), $w_{ij} = w_{ji}$ are symmetric empirical coefficients. The chemical potential of k-th end-member in solid solution (indexed as ss) can be formally written as:

$$\mu(S_k, \mathrm{ss}) = \mu_k^{\mathrm{ss}} = \mu_k^{\mathrm{oss}} + RT \ln \mathrm{a}_{\mathrm{k}}^{\mathrm{ss}} \qquad k = 1, 2 \ldots n+1 \tag{2}$$

On the other hand, it can be obtained from Eq.(1):

$$\mu(S_k, \mathrm{ss}) = \mu_k^{\mathrm{ss}} = \mu_k^{\mathrm{oss}} + \mathrm{RT} \ln \mathrm{x_k} + \sum_{i=1}^{n+1} w_{ki} x_i - \frac{1}{2} \sum_{i=1}^{n+1} \sum_{j=1}^{n+1} w_{ij} x_i x_j \qquad k = 1, 2 \ldots n+1 \tag{3}$$

The activity of S_k in the solid solution can be reached by comparing Eqs.(2) and (3):

$$a_k^{ss} = x_k \exp\left[\left(\sum_{i=1}^{n+1} w_{ki} x_i - \frac{1}{2} \sum_{i=1}^{n+1} \sum_{j=1}^{n+1} w_{ij} x_i x_j \right) \Big/ RT \right] = \gamma_k x_k \tag{4}$$

where γ_K is the molar activity coefficient. The last equation relates the empirical coefficients arranged in **w** matrix to the value of activity coefficient:

$$RT \ln \gamma_k = \sum_{i=1}^{n+1} w_{ki} x_i - \frac{1}{2} \sum_{i=1}^{n+1} \sum_{j=1}^{n+1} w_{ij} x_i x_j \tag{5}$$

Thermodynamics of Multicomponent Oxide Melt

We assume that the composition of the melt can described as a mixture of p components (e.g., oxides), identified as M_1, M_2, …, M_p, where $y(M_i)$ or y_i represents i-th component mole fraction. The matrix $\boldsymbol{\nu}$ of respective stoichiometric coefficients expresses the formation of each end-member from the melt components:

$$S_k = \sum_{j=1}^{p} \nu_{kj} \mathrm{M}_j \qquad k = 1,2 \ldots n+1 \tag{6}$$

According to Eq.(6), the chemical potential of the k-th end-member, S_k, in the melt (indexed as me) is given by:

$$\mu(\mathrm{S}_k, \mathrm{me}) = \mu_{Sk}^{\mathrm{me}} = \sum_{j=1}^{p} \nu_{kj} \mu(M_j, \mathrm{me}) = \sum_{j=1}^{p} \nu_{kj} \mu_j^{\mathrm{ome}} + RT \sum_{j=1}^{p} \nu_{kj} \ln a_{\mathrm{j}}^{\mathrm{me}} \qquad k = 1,2 \ldots n+1 \tag{7}$$

and the S_k activity in the melt can be expressed as[9]:

$$a(\mathrm{S}_k, \mathrm{me}) = a_{Sk}^{\mathrm{me}} = \prod_{j=1}^{p} \left(a_j^{\mathrm{me}}\right)^{\nu_{kj}} \tag{8}$$

The oxide activity in the melt, a_i^{me}, can be calculated using the equation[9]:

$$\log a(M_i) = \log a_i^{\mathrm{me}} = n_c(M_i) \log \left(\frac{n_c(M_i) y(M_i)}{\sum_{j=1}^{p} n_{\mathrm{c}}(M_j) y(M_j)} \right) + n_{\mathrm{o}}(M_i) \log\left[a\left(\mathrm{O}^{2-}\right)\right] \tag{9}$$

where $a(\mathrm{O}^{2-})$ is the activity of O^{2-} in a glassmelt, $n_{\mathrm{c}}(M_i)$ is the number of metal cation atoms, and $n_{\mathrm{o}}(M_i)$ is the number of oxygen atoms in a M_i-oxide formula.

Solidus - Liquidus Equilibria

Applying Eq.(2), we can express the molar Gibbs free energy of fusion of k-th end-member imbedded in the solid solution as:

$$\Delta_{\mathrm{fus}} G_{\mathrm{m}k} = \mu(S_k, \mathrm{me}) - \mu(S_k, \mathrm{ss}) = \Delta_{\mathrm{fus}} G_{\mathrm{m}k}^{\mathrm{o}} + RT \ln a_{Sk}^{\mathrm{me}} - RT \ln a_k^{\mathrm{ss}} \tag{10}$$

where the standard molar Gibbs free energy of fusion, $\Delta_{\mathrm{fus}}G^{\mathrm{o}}(\mathrm{m}, \mathrm{S}_k)$, corresponds to the congruent melting of the end-member S_k at temperature T. The following condition holds at equilibrium:

$$\Delta_{\mathrm{fus}} G_{\mathrm{m}k} = 0 \qquad k = 1,2 \ldots n+1 \tag{11}$$

whereas outside the equilibrium, i.e., in the sub/super-saturated melts, the affinity, A, to crystallization is given by[10]:

$$\mathrm{A} = \Delta_{\mathrm{fus}} G_{\mathrm{m}1} = \Delta_{\mathrm{fus}} G_{\mathrm{m}2} = \ldots = \Delta_{\mathrm{fus}} G_{\mathrm{m(n+1)}} \tag{12}$$

thus the thermodynamic driving force to melting/crystallization is the same for all the compounds forming the solid solution.

Let us suppose that the melt composition and chemical potentials of melt components are known. Then the Eq.(11) has to be solved with respect to the solid solution composition (given by mole fractions x_k) and, simultaneously, with respect to the liquidus temperature, T_{liq}. Due to the standard state definition as a pure compound or component at the system pressure and temperature, the temperature dependence of standard chemical potentials has to be considered. Because only the value of the standard molar Gibbs free energy of fusion is present in Eqs.(11) and (12), it is sufficient to know the temperature dependence of this quantity only. After several substitutions and simplification[9] we can obtain the relation analogous to the well-known LeChatelier-Schreder equation that we rearranged to the form:

$$\ln a_{\mathrm{k}}^{\mathrm{ss}} = \ln a_{Sk}^{me} + \frac{\Delta_{fus} H_{mk}^{o}}{R}\left(\frac{1}{T_{liq}} - \frac{1}{T_{fusk}^{\mathrm{o}}}\right) \qquad (13)$$

where $\Delta_{\mathrm{fus}}H_{\mathrm{mk}}^{\mathrm{o}}$ and $T_{\mathrm{fusk}}^{\mathrm{o}}$ are the standard molar enthalpy and temperature of fusion of the k-th end member, S_{k}, respectively.

CALCULATIONS AND RESULTS

We began to test our model focusing on its ability to predict the composition of spinel solid solutions crystallizing at T_{liq}. For the testing we developed a special software in FORTRAN and applied it to the experimental data available in the database of HLW glasses comprising glass compositions and T_{liq} as well as the composition of spinel crystals precipitating at temperatures close to T_{liq} in 5 different HLW glassmelts[11].

In the glassmelt, there is an equilibrium between Fe^{2+} and Fe^{3+} effecting spinel crystallization. Because the content of iron oxide in the glassmelts, from our database, was formally expressed as $\mathrm{Fe_2O_3}$, we estimated the redox ratio $y(\mathrm{FeO})/y(\mathrm{Fe_2O_3})$ using the empirical equation proposed by Baucke[12]:

$$\log\frac{y(\mathrm{Fe}^{2+})}{y(\mathrm{Fe}^{3+})} = 3.2 - 6.5\Lambda \qquad (14)$$

were Λ is the optical basicity that we calculated from the melt composition[9, 13]. Because Eq.(14) holds for the thermodynamic temperature of 1673 K at oxygen partial pressure $P(\mathrm{O_2}) = 21.278\cdot10^3$ Pa, i.e., at ambient air atmosphere, we recalculated[9] the redox ratio for our melt temperature using the value of (172±42) kJ.mol^{-1} reported by Schreiber *et al.*[14] as the standard molar reaction enthalpy of the reaction $\mathrm{Fe}^{3+}+\frac{1}{2}\,\mathrm{O}^{2-} = \mathrm{Fe}^{2+}+\frac{1}{4}\,\mathrm{O_2}$:

$$\log\left[\frac{y(Fe^{2+})}{y(Fe^{3+})}\right] = 8.5704 - 6.5\Lambda - \frac{8984.68}{T} \qquad (15)$$

Having the glassmelt composition at T_{liq}, we calculated a_i^{me} from Eq.(9) and the needed $a(\mathrm{O}^{2-})$ value was, according to Pyare and Nath[15], estimated by the relation:

$$a(\mathrm{O}^{2-}) = \gamma(\mathrm{O}^{2-})\cdot 10^{(-2.035+4.356\Lambda)} \qquad (16)$$

where $\gamma(\mathrm{O}^{2-})$ is a constant approximated[9, 15] by the value 0.14. Then applying Eq.(8), we obtained a_{Sk}^{me} from which a_k^{ss} can be calculated using Eq.(13). The parameters $\Delta_{\mathrm{fus}}H_{\mathrm{mk}}^{\mathrm{o}}$ and $T_{\mathrm{fusk}}^{\mathrm{o}}$ used in our calculations are listed in Table 2[9].

Table 2. Parameters from Eq.(13)[9]

	S_1 (FN)	S_2 (FF)	S_3 (NC)	S_4 (FC)
$T_{\mathrm{fus}}^{\mathrm{o}}$ [K]	2191	1870	2598	2423
$\Delta_{\mathrm{fus}}H_m^{\mathrm{o}}$ [kJ/mol]	161.78	138.07	191.83	178.90

To calculate the mole fraction of S_k in the spinel solid solution, x_k, we had to determine the symmetrical **w** matrix containing 10 unknown elements. To do that, we take advantage of analytically measured compositions of spinel crystals, expressed as mole fractions of Cr^{3+}, Ni^{2+}, and total Fe, precipitating in 5 glassmelts at T close to T_{liq}. Because we did know the Fe^{2+}/Fe^{3+} ratio, we could not calculate directly x_k from the analytical composition. Knowing a_k^{ss}, we constructed the system of 20 equations (4 equations for each spinel composition), according to Eq.(4), with 10 unknown variables (the elements of the **w** matrix), where x_k was taken as a parameter that was varied within given limits with the step 0.01. The limits for x_k were determined from the analytical composition supposing that the spinel structure is stoichiometric. The system of equations was solved by using the least square method for each composition (x_k) yielding the elements of the **w** matrixes. Then we take each composition (x_k) along with the corresponding **w** matrix and calculated the a_k^{ss} values and the sum of squares of the differences between these values and the a_k^{ss} values estimated from the melt composition. As the best approximation of the **w** matrix, we take the solution giving the lowest sum of squares ($SSE = 0.5 \cdot 10^{-6}$):

$$w = \begin{bmatrix} -193860 & -48961 & -182000 & -231000 \\ -48961 & -513210 & -121660 & -193710 \\ -182000 & -121660 & -287520 & -297500 \\ -231000 & -193710 & -297500 & -344310 \end{bmatrix} \tag{17}$$

Table 3 shows the calculated composition of spinel solid solutions, x_k, precipitating in 5 different glassmelts together with their analytical composition. Knowing the x_k, we could estimate the expected content of Fe^{2+} and Fe^{3+} in the solid solution.

Table 3. Analytical and Calculated (x_k) Compositions of Spinel Solid Solutions

Glass	Cr^{3+}	Ni^{2+}	Fe^{total}	x_1 (FN)	x_2 (FF)	x_3 (NC)	x_4 (FC)	Fe^{2+}_{calc}	Fe^{3+}_{calc}
SP-1	18	26	56	0.730	0.000	0.050	0.220	7.33	48.67
SP-Si-1	6	21	73	0.621	0.289	0.009	0.081	12.40	60.60
SP-Si-3	47	18	35	0.295	0.000	0.245	0.460	15.33	19.67
MS-4	32	26	42	0.520	0.000	0.260	0.220	7.33	34.67
MS-7	51	13	36	0.000	0.235	0.390	0.375	20.33	15.67

CONCLUSIONS

The proposed model is able to estimate the composition of spinel solid solutions precipitating in HLW glassmelts. We are able to calculate the activities of spinel end-members in the glassmelts from their composition. To do the same for the solid solution, we determined the elements of the **w** matrix suggested for the calculation of the activity coefficients of end-members in the solution. These coefficients enable the calculations of end-members activities in the solution from its composition and vice versa. Both activities are necessary for the estimation of the affinity to crystallization which we will use for the prediction of spinel concentrations in HLW glassmelts and spinel crystallization kinetics.

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