THE EFFECT OF SPINEL SLUDGE AGING ON ITS VISCOSITY

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Spinel sludge samples of different age were prepared by allowing spinel to settle in alumina crucibles. During the aging process the concentration of spinel crystals increased, which resulted in higher viscosity of the sludge. To quantify this process, we suggested functions describing dependence of sludge viscosity on spinel concentration, time dependence of spinel concentration in the sludge, and the dependence of sludge viscosity on sludge age.

INTRODUCTION

High-level nuclear waste (HLW) located at Hanford and Savannah River sites will be immobilized by vitrification technology converting the HLW slurry into a safe solid form. Economic concerns require achieving a waste content in glass as high as possible. The waste is rich in Fe_2O_3 that together with other waste components, NiO and Cr_2O_3, form spinel-type crystals (Fe,Ni)$(Fe,Cr)_2O_4$ if their solubility limits in particular glass are exceeded [1]. The crystals have approximately 1.9 times higher density than the glass-melt and will settle in a melter, if they are large enough, forming a sludge layer on the melter bottom. Such layer could shorten the melter's lifetime obstructing the flow of a melt in narrow parts of the melter. The possible solution might be the periodical removing of the sludge. For such technology, it is necessary to know the rheological behavior of the sludge. This knowledge is also useful for the prediction of spinel sludge accumulation on the inclined walls of the HLW melter by mathematical modeling [2].

EXPERIMENTAL

We chose the same glass SS-AA for experiments as in our previous study on spinel sludge rheology [3]. This glass was formulated to precipitate a high amount of spinel crystals. Therefore, it had a high content of Cr_2O_3 that strongly increases liquidus temperature, T_L, [4] and NiO that significantly increases T_L and the concentration of spinel crystals [5]. The chemical composition of the glass is presented in table 1. Using partial specific liquidus temperatures for the glass components [4], we estimated T_L to be 1344 °C. Table 1 also lists the composition of the glass SS-AB which does not precipitate spinel. For this reason it has no Cr_2O_3, NiO, and MnO and Fe_2O_3 was substantially reduced. The other glass components are in the same proportions as in the SS-AA glass.

We batched the glass using analytical-grade chemicals (oxides, carbonates, and boric acid) and melted at 1350 °C for 1 h. Then the glass was quenched, crushed, milled and remelted for another 1 h at the same temperature. We prepared the samples of spinel sludge in an alumina crucible by allowing spinel to settle from molten glass SS-AA at 1100 °C. We prepared two sludge samples for our study. Sample SV1 was made by the spinel settling for 5 days and sample SV2 by allowing spinel to settle for 25 days. To determine concentra-

Table 1. Composition of the glass SS-AA and SS-AB (wt.%).

Oxide	SS-AA	SS-AB
Li_2O	2.93	3.38
Na_2O	15.37	17.72
MgO	2.11	2.43
MnO	0.35	0.00
NiO	3.21	0.00
B_2O_3	6.84	7.89
Al_2O_3	7.82	9.01
Cr_2O_3	1.50	0.00
Fe_2O_3	14.93	7.73
SiO_2	44.94	51.84

tion of crystals, we applied quantitative X-ray powder diffraction (XRD) analysis using Co-K_α radiation. The effect of spinel sludge aging on its rheology was measured using a rotating spindle viscometer (figure 1) in the temperature range from 650 to 1100 °C. The cylindrical spindel in this viscometer was different from the disk-shaped spindel used in our previous work [3].

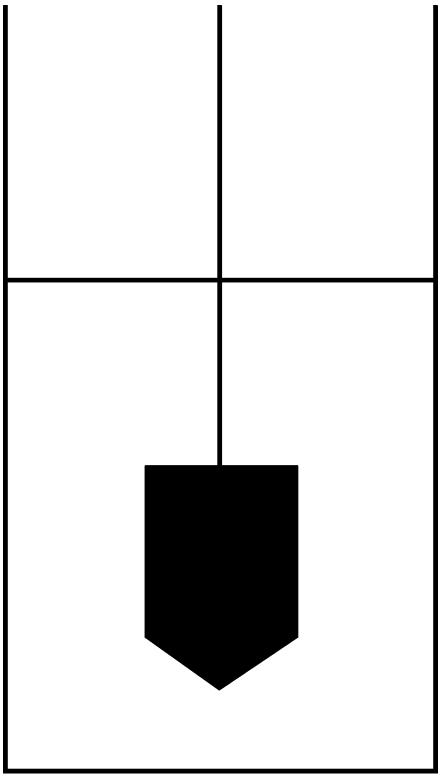

Figure 1. Schematic setup of the rotating spindle viscometer.

RESULTS AND DISCUSSION

Both sludge samples were examined by XRD. Spinel mass concentrations were determined using standard glass with known spinel content. To calculate volume concentration, we measured density of both samples. The density of spinel crystals is 5.140 g/cm^3. Results presented in table 2 show that the spinel concentration in sludge increased with time. Sample SV1 contained 11.3 vol.% and sample SV2 17.0 vol.% of spinel crystals. These values are plotted in figure 2 and their dependence on time was fitted by the function:

$$f = \Phi[1 - \exp(-\tfrac{\tau}{\tau_x})] \qquad (1)$$

where f is the volume fraction, τ is the time, and Φ and τ_x are constants estimated by the least square method. Constant Φ represents the limit value of f when $\tau \to \infty$.

Table 2. Spinel sludge density and spinel concentration (volume fractions).

Sample	τ (days)	ρ (g cm^{-3})	f
SV1	5	2.757	0.113
SV2	25	2.967	0.170

The spinel-fraction curve in figure 2 indicates that the spinel concentration increased much faster at the beginning and its slope, df/dτ, decreased with time. After 25 days the concentration was quite close to the saturated value represented by Φ.

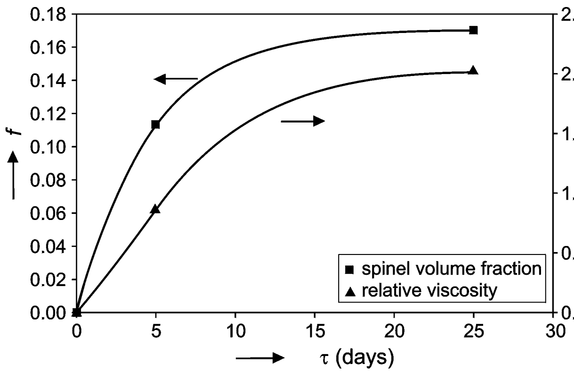

Figure 2. Dependence of spinel volume fraction and relative viscosity on time fitted by equations (1) and (5).

We analyzed the rheological behavior of both sludge samples by plotting their shear stress data versus the corresponding shear rates for different constant temperatures. These dependencies were linear and time--independent. Thus, both samples behaved as Newtonian liquids without any significant deviations. This behavior was different from what we had observed in the previous work [3]. It is possible that the cylindrical shape of the spindel we used in this study could cause such difference. The different geometry and thus the different radial distribution of the shear rate resullted in diminishing the non-Newtonian character of our heterogeneous two-phase system. From the shear stress and shear rate data we calculated viscosity. We fitted its temperature dependence using the equation:

$$\log\eta = At^B \qquad (2)$$

where η is the viscosity in dPa s, t is the temperature in °C, A and B are constants, the values of which are listed in table 3. Table 4 shows the calculated values of $\log\eta$ for samples SV1 and SV2. The viscosity curves in figure 3 indicate that sludge viscosity increased during aging. This effect is caused by the increasing concentration of spinel crystals because the presence of this solid phase increases the internal friction of the heterogeneous mixture. For example at 1094 °C the viscosity of sludge SV1 was 2.379 times higher than the viscosity of glass SS-AB, which had viscosity η_0 = 119 dPa s at 1094 °C [3]; SV2 sludge had viscosity 7.553 times higher than that of the glass. To express this viscosity change at constant temperature, we used the relative viscosity, η_r, defined as:

$$\ln \eta_r = \ln\left(\frac{\eta}{\eta_0}\right) \tag{3}$$

where η_0 is the viscosity of the glass without spinel crystals (i.e. SS-AB). The dependence of η_r on f, plotted in figure 4, was fitted using the equation recommended by Mooney [6]:

$$\ln \eta_r = \frac{\alpha f}{1-\beta f} \tag{4}$$

where α and β are constants listed in table 5, Their values were calculated using the least square method. Figure 5 shows that for f >0.1 the slope, $d\eta_r/df$, starts to significantly increase with increasing f and this higher viscosity substantially hinders the settling of crystals. This agrees with the decline of $df/d\tau$ seen in figure 2. Substituting equation (1) into equation (4) we obtain the dependence of η_r on τ (figure 2):

$$\ln \eta_r = \frac{\alpha\Phi[1-\exp(-\frac{\tau}{\tau_x})]}{1-\beta\Phi[1-\exp(-\frac{\tau}{\tau_x})]} \tag{5}$$

For long times when $\tau \to \infty$ the ln η_r, reaches its limit value ln η_r^∞:

$$\ln \eta_r^\infty = \frac{\alpha\Phi}{1-\beta\Phi} \tag{6}$$

When we introduce the fraction, p, defined as:

$$p = \frac{\ln \eta_r}{\ln \eta_r^\infty} \tag{7}$$

we can predict time needed for the sludge to reach the viscosity p ln η_r^∞:

$$\tau = \tau_x \ln\left(\frac{1-\beta\Phi + p\beta\Phi}{1-\beta\Phi - p + p\beta\Phi}\right) \tag{8}$$

where $p \in$ <0,1> represents the fraction of the limit value ln η_r^∞. Several examples are listed in table 6.

Table 3. Coefficients from equation (2).

sludge	A	B
SV1	662445	-1.78730
SV2	205678	-1.59355

Table 4. Calculated viscosity of SV1 and SV2 sludge samples using equation (2).

t (°C)	log η (η in dPa s)	
	SV1	SV2
650	6.217700	6.771264
700	5.446357	6.017026
750	4.814518	5.390561
800	4.289998	4.863723
850	3.849456	4.415830
900	3.475619	4.031389
950	3.155473	3.698592
1000	2.879054	3.408300
1050	2.638628	3.153346
1100	2.428112	2.928037

Table 5. Parameters from equations (1) and (4).

parameter	
α	4.50122
β	3.65618
Φ	0.17076
τ_x	4.61251

Table 6. Calculated time to reach the p fraction of η_r^∞.

p	τ (days)
0.50	6.0
0.75	10.1
0.95	18.2
0.98	22.5

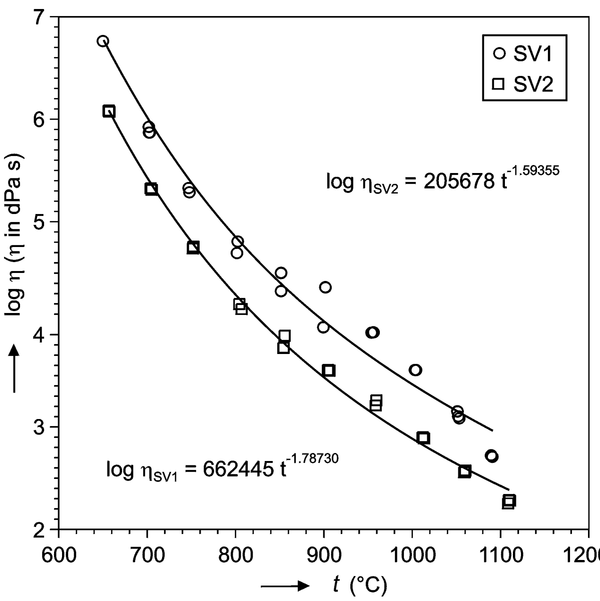

Figure 3. Temperature dependence of viscosity for spinel sludge samples SV1 and SV2.

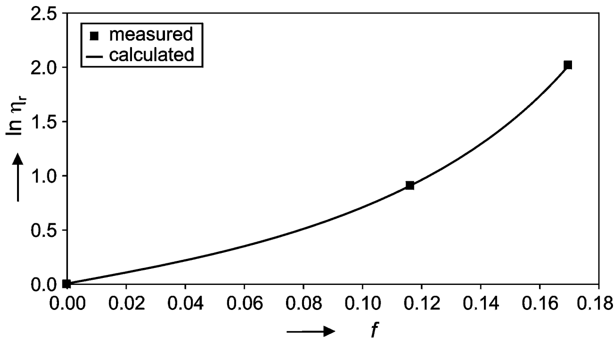

Figure 4. Dependence of sludge relative viscosity on spinel volume fraction at 1094 °C fitted by equation (4).

CONCLUSION

By allowing spinel to settle in glass for 5 and 25 h, we prepared two sludge samples of different age. As the sludge aged, its density and crystal concentration increased. This increase resulted in a higher sludge viscosity that was slowing down spinel settling and densification of the sludge. For quantification of these effects, we suggested equations for predicting sludge viscosity during aging at constant temperature (1094 °C). The most significant change of viscosity (75% of the final value, ln η_r^∞) occurred during the first 10 days and, e.g., 95% of the final viscosity value, was reached in approximately 18 days.

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VLIV STÁRNUTÍ SPINELOVÉ SEDLINY NA JEJÍ VISKOZITU

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Sedimentací spinelových krystalů ve sklovině po dobu 5 a 25 dní byly připraveny dva vzorky spinelové sedliny. Kvantitativní rentgenovou difrakční analýzou byla určena koncentrace spinelu v sedlinách. Stárnutí sedliny se projevilo růstem koncentrace spinelových krystalů, což mělo za následek zvýšení viskozity sedliny. Pro popis těchto závislostí byly navrženy funkce vystihující závislost koncentrace spinelu na čase, závislost relativní viskozity sedliny na koncentraci spinelu a na čase. Byly odhadnuty časy stárnutí sedliny způsobující zvýšení logaritmu její relativní viskozity na hodnotu 50, 75, 95 a 98% z konečné hodnoty viskozity.