RHEOLOGY OF SPINEL SLUDGE IN MOLTEN GLASS

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Spinel sludge, which forms while vitrifying high-level waste, obstructs the flow of molten glass and damages the melter. The effectiveness of removing spinel sludge from a high-level waste glass melter depends on its rheological behavior. We prepared spinel sludge in a laboratory crucible by allowing spinel to settle from molten glass and measured the response of the sludge to shear using a rotating spindle viscometer. The shear stress increased nonlinearly with the velocity gradient (the shear rate) and with time at a constant velocity gradient, as is typical for a pseudoplastic rheopectic liquid. The apparent viscosity of the sludge substantially increased when RuO_2 needles were present.

INTRODUCTION

Spinel $(Ni,Fe,Mn)(Cr,Fe)_2O_4$ is a ubiquitous crystallization form that precipitates from high-level waste glasses containing Fe_2O_3, Cr_2O_3, and NiO [1-4]. It nucleates virtually instantaneously and grows rapidly [5]. Spinel is harmless when it precipitates in glass during cooling. It does not cause cracking nor does it reduce glass durability [6]. However, spinel can cause serious problems in glass melters. Formation of spinel sludge at the melter bottom or precipitation of spinel in the melter overflow can obstruct the discharge of glass and shorten the melter lifetime [7]. Economic concerns may require an increase in the loading factor of the waste in glass. At a certain level of waste loading, spinel precipitates in the melter. If some fraction of spinel settles and accumulates at the melter bottom, a periodical removal of spinel sludge may be considered. Construction of melters with inclined bottoms and bottom drains has been proposed [8]. The knowledge of rheological behavior of precipitated spinel sludge is important for an advanced melter design. In this work, we produced spinel sludge in the laboratory and studied its behavior using a rotating spindle viscometer.

EXPERIMENTAL PART

We used three glasses (table 1). The baseline glass (SS-A) had high concentrations of Fe_2O_3, Cr_2O_3, and NiO and a large number of minor components. Most of the minor components were absent in its simplified version (SS-AA) that had an identical composition in terms of major components. While SS-A and SS-AA were designed to precipitate spinel, SS-AB was formulated to produce a similar composition that does not precipitate spinel. It had all minor components deleted, including those that form spinel, and its Fe_2O_3 content was reduced to almost one half. The major components, SiO_2, B_2O_3, Na_2O, Li_2O, MgO, and Al_2O_3, were in identical proportions in all three glasses.

Table 1. Composition of glasses (wt.%).

oxide	SS-A	SS-AA	SS-AB
SiO_2	42.38	44.94	51.83
B_2O_3	6.45	6.84	7.89
Na_2O	14.49	15.37	17.72
Li_2O	2.77	2.93	3.38
MgO	1.99	2.11	2.43
Al_2O_3	7.37	7.82	9.01
Fe_2O_3	14.08	14.93	7.73
Cr_2O_3	1.42	1.50	0.00
MnO	0.33	0.35	0.00
NiO	3.03	3.21	0.00
Ag_2O	0.06	0.00	0.00
BaO	0.28	0.00	0.00
CaO	0.93	0.00	0.00
CdO	0.64	0.00	0.00
CeO_2	0.06	0.00	0.00
Cl	0.01	0.00	0.00
Co_2O_3	0.08	0.00	0.00
CuO	0.03	0.00	0.00
F	0.06	0.00	0.00
K_2O	0.26	0.00	0.00
La_2O_3	0.25	0.00	0.00
MoO_3	0.10	0.00	0.00
Nd_2O_3	0.17	0.00	0.00
P_2O_5	0.43	0.00	0.00
PbO	0.16	0.00	0.00
Rh_2O_3	0.03	0.00	0.00
RuO_2	0.03	0.00	0.00
Sb_2O_3	0.06	0.00	0.00
SeO_2	0.08	0.00	0.00
SO_3	0.18	0.00	0.00
SrO	0.03	0.00	0.00
TiO_2	0.03	0.00	0.00

We batched the glasses using analytical-grade chemicals and melted them at 1350 °C. We estimated liquidus temperatures (T_L) using a spinel-based first-

-order model [9] and obtained T_L = 1520 °C for SS-A and 1344 °C for SS-AA. We made spinel sludge by heat treating glasses for 5 days at 1100 °C in 95%-silica crucibles. Then we smashed the crucibles to pieces and carefully separated the sludge from the spinel-free glass. We measured sludge viscosity using a Brookfield digital rotating spindle viscometer (Model DV-II) in the temperature range from 1094 to 1393 °C starting from lower temperatures.

RESULTS AND DISCUSSION

The sludge consisted of agglomerations of cubic black crystals of spinel (figure 1). In SS-A glass, RuO_2 needle-like crystals (figure 1b) reinforced the agglomerates. The fraction of spinel in the sludge estimated by XRD was roughly 12 vol.%. The apparent viscosity of the sludge and the sludge-free glass is shown in table 2. Glass behavior was Newtonian, showing no dependence of apparent viscosity (η_a) on effective velocity gradient (∇v_{ef}) and time (t). The η_a of sludge increased with t, but this time-dependence weakened as temperature (T) increased until the η_a became time-independent. SS-A sludge reached this point at 1350 °C, when η_a was < 6 Pa s, and SS-AA sludge reached this point at 1300 °C, when η_a was < 5 Pa s. This behavior was probably caused by spinel dissolution that breaks down spinel agglomerates. The higher η_a of SS-A sludge as compared to SS-AA sludge can be attributed to the presence of RuO_2 needles in SS-A sludge.

Figure 2 displays effective shear stress (τ_{ef}) versus ∇v_{ef} for SS-A sludge at different temperatures. The η_a decreases as ∇v_{ef} increases. This behavior is typical for pseudoplastic liquids. The idle time between each subsequent measurement at a higher temperature was 30 min. The second measurement at 1293 °C was carried out after the series of measurements starting at 1094 °C and ending at 1393 °C was completed. The lower τ_{ef} from the second measurement indicates that the preceding heat treatment and deformation weakened the sludge structure. To separate the effect of spinel dissolution from the structural weakening caused by deformation, the second measurement at 1342 °C was performed immediately after the first one. The decrease in τ_{ef} was smaller, but the structural weakening by flow was significant.

The effect of t, ∇v_{ef}, T, and idle time on structural changes is shown in figures 3 and 4. Figure 3 displays τ_{ef} as a function of time for different values of ∇v_{ef} and T (∇v_{ef} was increased as η_a decreased to allow shear-stress reading). The τ_{ef} values increased with time for all ∇v_{ef} values, a behavior typical for a rheopectic liquid. Idling to switch spindle velocity was negligible, but it took 20 minutes to increase and stabilize a new temperature. This time probably was not long enough for the agglomerated structure to completely rearrange at T < 1193 °C as can be seen from figure 4.

Figure 4 displays the τ_{ef} increase as a function of time at 1193 °C and a constant ∇v_{ef} = 0.01 s^{-1}. The initial measurement is labeled “start.” In subsequent measurements, the structure was allowed to reassemble from 1 to 30 min. The η_a increased with time for each subsequent measurement. This can be attributed to the development of denser agglomeration when the sludge

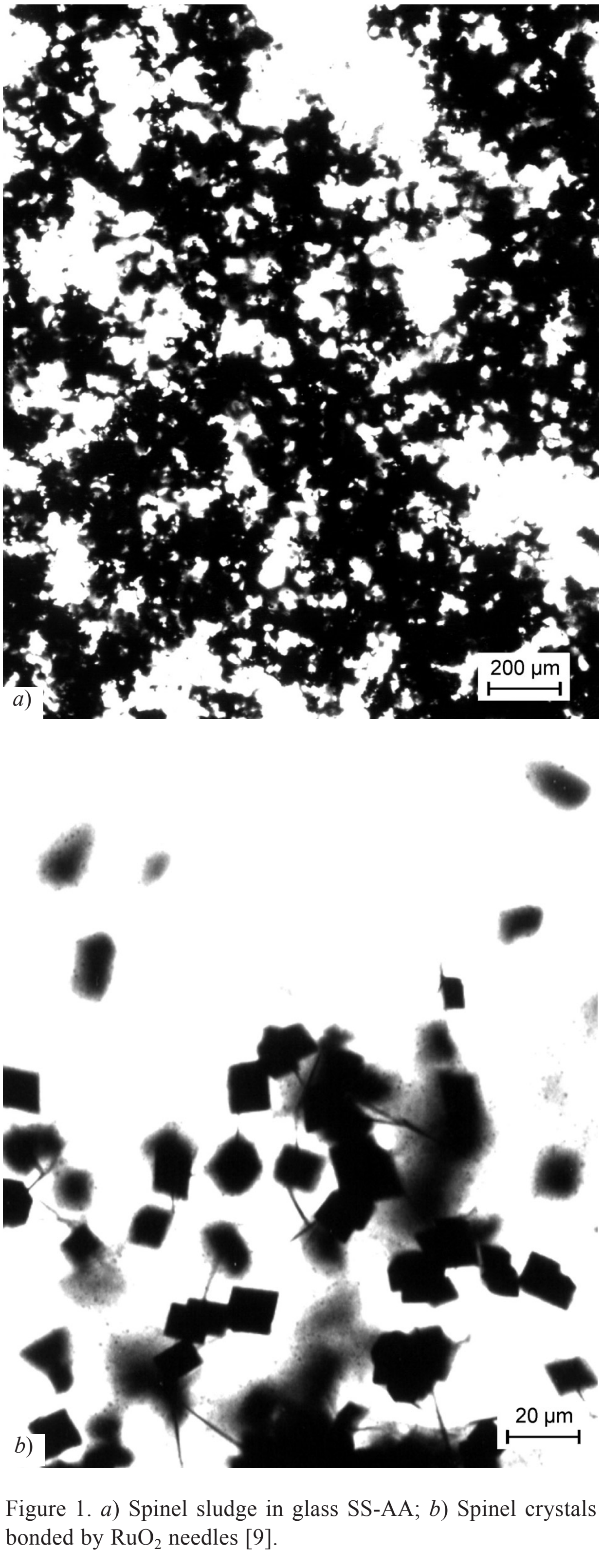

Figure 1. *a*) Spinel sludge in glass SS-AA; *b*) Spinel crystals bonded by RuO_2 needles [9].

Table 2. Apparent viscosity of spinel sludge and glass at the beginning ($\eta_{a,0}$) and after 15 minutes of shearing ($\eta_{a,15}$).

temperature (°C)	effective velocity gradient ∇v_{ef} (s^{-1})	apparent viscosity ($Pa.s^{-1}$)					
		SS-A (sludge)		SS-AA (sludge)		SS-AB (glass)	
		($\eta_{a,0}$)	($\eta_{a,15}$)	($\eta_{a,0}$)	($\eta_{a,15}$)	($\eta_{a,0}$)	($\eta_{a,15}$)
1094	0.005	201.4	225.8			11.9	11.9
1143	0.010	92.3	102.0			7.7	7.7
1193	0.010	56.0	72.0	11.4	17.1	5.0	5.0
1243	0.025	21.9	31.4			3.7	3.7
1293	0.050	11.6	13.8	5.0	5.6	2.6	2.6
1342	0.050	6.6	6.7			1.8	1.8
1393	0.050	2.7	2.7				

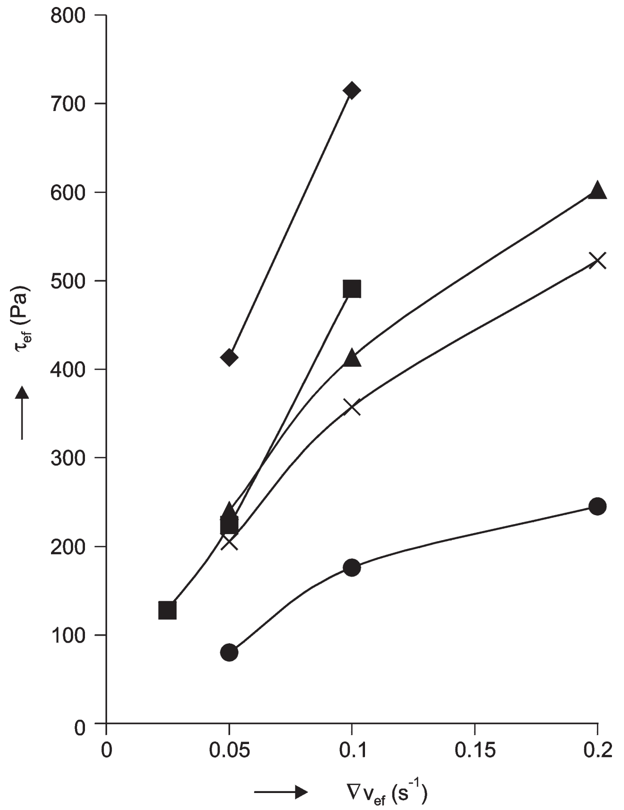

Figure 2. Dependence of τ_{ef} on ∇v_{ef} for SS-A sludge. Numbers 1 and 2 in the legend represent the first and second measurement at the same temperature.
◆ - 1293 °C, first measurement, ■ - 1293 °C, second measurement, ▲ - 1342 °C, first measurement, x - 1342 °C, second measurement, ● - 1393 °C, first measurement.

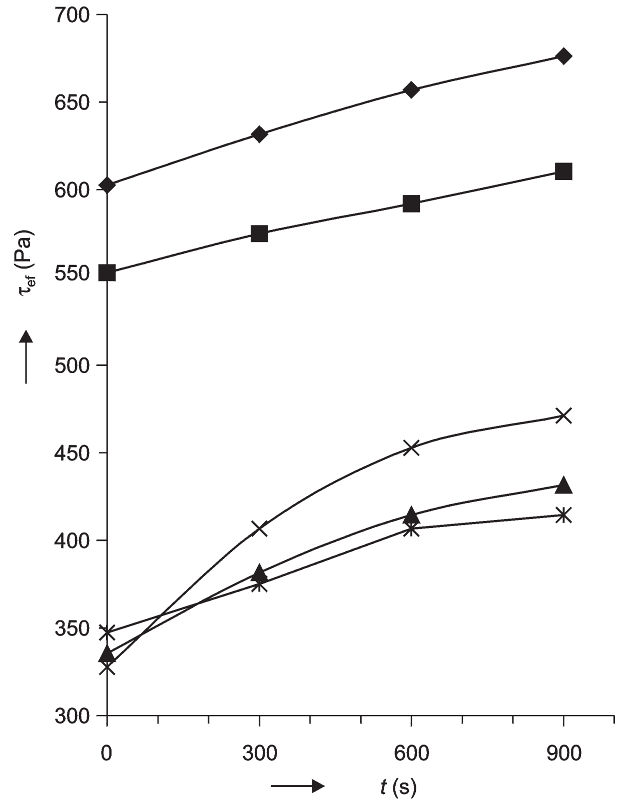

Figure 3. Dependence of τ_{ef} on t at different temperatures (in °C) and ∇v_{ef} values for SS-A sludge.
◆ - 1094 °C, ∇v_{ef} = 0.005 s^{-1}, ■ - 1143 °C, ∇v_{ef} = 0.010 s^{-1}, ▲ - 1193 °C, ∇v_{ef} = 0.010 s^{-1}, x - 1243 °C, ∇v_{ef} = 0.025 s^{-1}, ∗ - 1293 °C, ∇v_{ef} = 0.050 s^{-1}

was sheared. During idling, when shearing stops, the agglomerates tend to get looser. Therefore, a new measurement started with a lower viscosity. The measured dependence of τ_{ef} on t was fitted by the equation:

$$\tau_{ef} = \tau_1 + \tau_2 \left[1 - \exp\left(-\frac{t}{t_r}\right)\right] \quad (1)$$

where τ_1 and τ_2 are constants (τ_1, τ_2>0), and t_r (t_r >0) is the retardation time. The τ_1 decreases and the τ_2 increases as the idle time (t_i) increases (figure 5), while the sum $\tau_1 + \tau_2$ ($\tau_{ef} \rightarrow \tau_1 + \tau_2$ as $t \rightarrow \infty$) is nearly constant. The t_r decreases as the t_i decreases (figure 6), resulting in a steeper increase of τ_{ef} with time.

At η_a values higher than 7 Pa s, the apparent viscosity of sludge increased with time at constant ∇v_{ef}

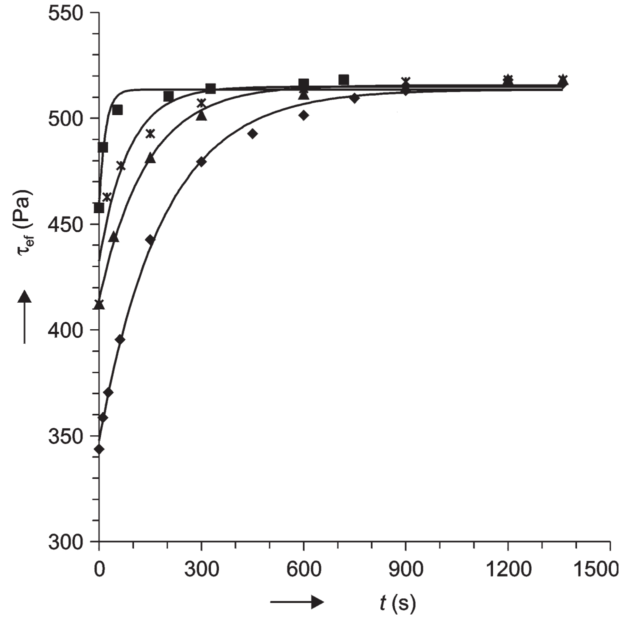

Figure 4. Dependence of τ_{ef} on t for different idle times at T = 1193 °C and ∇v_{ef} = 0.01 s^{-1} for SS-AA sludge.
◆ - start, ■ - 60 s, x - 600 s, ▲ - 1800 s.

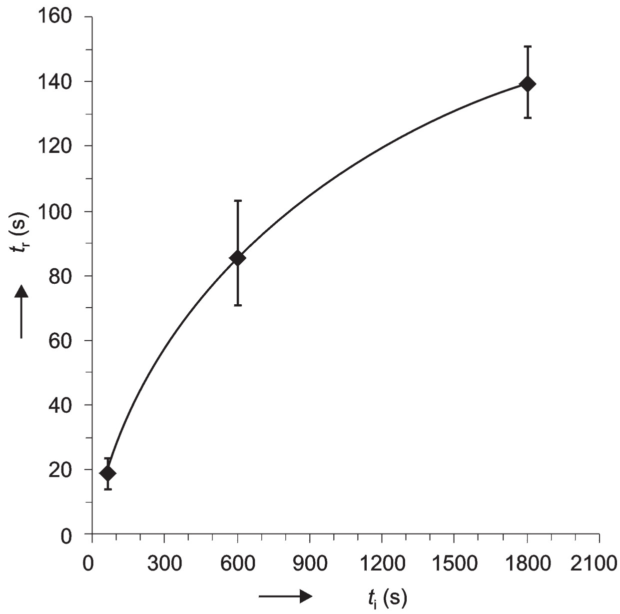

Figure 6. Dependence of the retardation time (t_r) on the idle time (t_i).
◆ - t_r = 189(1 - exp(-$t_i^{0.735}$/182.5))

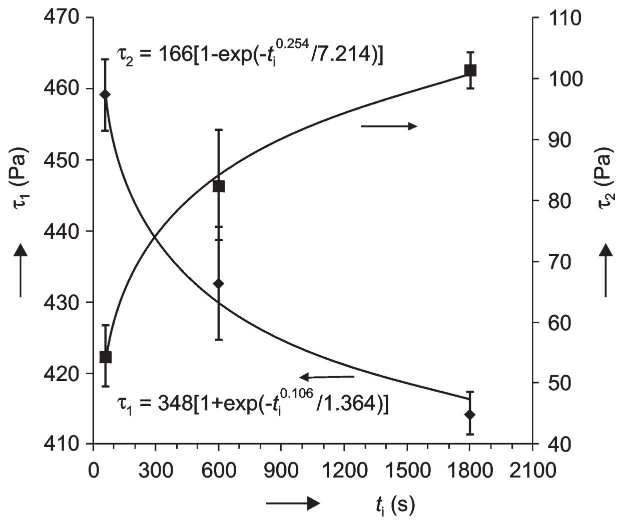

Figure 5. Dependence of the parameters τ_1 and τ_2 from equation (1) on the idle time (t_i).
◆- τ_1 = 348(1 + exp(-$t_i^{0.106}$/1.364)),
■ - τ_2 = 166(1 + exp(-$t_i^{0.254}$/7.214))

in the range from 0.005 to 0.05 s^{-1}. This was probably caused by agglomeration of spinel crystals around the spindle. In the range from about 3 to 7 Pa s, viscosity decreased with increasing ∇v_{ef} in the range from 0.05 to 0.2 s^{-1}, probably because the fast-rotating spindle breaks down the sludge structure formed by crystals with partially dissolved contacts.

CONCLUSIONS

Spinel sludge from high-level waste glass behaves as a rheopectic pseudoplastic liquid. Its τ_{ef} is an increasing function of ∇v_{ef} and time. At constant T and ∇v_{ef}, the rotating spindle progressively affects the structure of the surrounding sludge, causing a higher friction and increasing τ_{ef} with time until a new equilibrium is reached. As ∇v_{ef} and T increase, the sludge structure rearranges, the η_a decreases, and a new equilibrium structure is formed. RuO_2-free sludge approached time-independent behavior above 1300 °C. The sludge containing RuO_2 approached time-independent behavior above 1350 °C. At 1094 °C, η_a was roughly 19 times higher than that of sludge-free glass, but only 2 to 4 times higher at temperatures at which it became time-independent.

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References

1. Jain V.: Ceram. Trans. *29*, 523 (1993).
2. Kim D.-S., Hrma P.: Ceram. Trans. *45*, 49 (1994).
3. Schweiger M.J., Stachnik M.W., Hrma P.: Ceram. Trans. *87*, 335 (1998).

4. Lamont M.J., Hrma P.: Ceram. Trans. *87*, 343 (1998).
5. Reynolds J.G., Hrma P.: *Scientific Basis for Nuclear Waste Management* (Editors W.J. Gray and I.R. Triay) *465*, p.65, Material Research Society, Pittsburgh, Pennsylvania, 1997.
6. Kim D.-S., Peeler D.K., Hrma P.: Ceram. Trans. *61*, 177 (1995).
7. Bunnell L.R.: *Laboratory Work in Support of West Valley Glass Development*, PNL-6539, Pacific Northwest Laboratory, Richland, Washington, 1988.
8. Elliott M.L., Shafer P.J., Lamar D.A., Merrill R.A., Grunewald W., Roth G., Tobie W.: *Hanford High-Level Waste Melter System Evaluation Data Packages*, PVTD-C95-03.01C4, Pacific Northwest Laboratory, Richland, Washington, 1995.
9. Mika M., Schweiger M.J., Hrma P., Vienna J.D.: *Scientific Basis for Nuclear Waste Management* (Editors W.J. Gray and I.R. Triay), *465*, p.71, Material Research Society, Pittsburgh, Pennsylvania, 1997.

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REOLOGIE SPINELOVÉ SEDLINY VE SKLOVINĚ

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Spinelová sedlina, která vzniká při vitrifikaci vysoce aktivních odpadů, brání v toku sklovině a ničí tavicí agregát. Efektivnost odstraňování spinelové sedliny z tavicího agregátu pro vysoce aktivní odpady závisí na jejím reologickém chování. V laboratorním kelímku jsme připravili spinelovou sedlinu tak, že jsme nechali spinel usazovat ve sklovině, a za použití rotačního viskozimetru jsme měřili odezvu na smykovou deformaci. Smykové napětí vzrůstalo nelineárně s gradientem smykové rychlosti (rychlostí smykové deformace) a s časem při konstantním gradientu smykové rychlosti, jak je to typické pro pseudoplastickou reopektní kapalinu. Zdánlivá viskozita sedliny podstatně vzrostla, když byly přítomny jehličky krystalů oxidu RuO_2.