VISCOSITY OF CALCIUM FERRITE SLAGS AND CALCIUM ALUMINO-SILICATE SLAGS CONTAINING SPINEL PARTICLES

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ABSTRACT

The viscosity of a 19 wt%CaO-81 FeOx melt containing Fe_3O_4 particles up to a volume fraction of 0.1 was measured and compared with a previous study of the viscosity of 10 wt% Al_2O_3-28 CaO-10 MgO-42 SiO_2 slag containing up to 0.2 volume fraction of $MgAl_2O_4$. The viscosity of both the alumino-silicate slag/spinel and the calcium ferrite/magnetite mixtures increased as the volume fractions of particles increased. The mixtures all showed apparent "Bingham" behaviour.

The results will be discussed in terms of predicting two-phase liquid behaviour.

INTRODUCTION

The viscous properties of slags with suspended particles are of practical importance to many metal smelting and refining processes. Examples where solids in slags may influence the liquid behaviour include magnetite formation during the copper making process, which can happen if the conditions becomes too oxidising at the operating temperature and the slag starts to precipitate solid magnetite (Fe_3O_4). Another example is when water-cooling is used to chill a refractory lining from the slag. The behaviour of the liquid/solid mixture in the mushy zone between the frozen and liquid slag may have an effect on the flow patterns in the furnace. Solid suspension in slags can cause significant change to the flow properties of the molten slag, impacting on the smooth operation of the process. The viscosity of solid-containing slags is therefore clearly of interest to smelter operators.

The viscosity of liquid-solid mixtures has been extensively studied at room temperature, but very little work has been done on high temperature systems. There has been a study on a molten salt at 200°C containing a suspension of glass spheres or fibres[1], and a study on molten Al-Cu alloys containing solid particles[2,3]. There have been several studies of viscosity of natural lavas and magmas containing solid crystals[4-6], but these studies generally lack an accurate knowledge of the volume fraction of crystals and the composition of the melt will have varied with temperature. Similar approaches have been used to investigate synthetic slags in the sub-liquidus region with a recent approach using micrographic techniques to determine the volume fraction of solids[7]. There has been a study [8] of the behaviour of spherical crystals suspended in a high viscosity glass matrix (10^8 and 10^{14} Pa s) where the viscosity of glassy $Mg_3Al_2Si_3O_{12}$, containing spherical crystals with solid volume fractions up to nearly 70 % was measured. The volume fraction was easily determined from either density measurement or by micrographic analysis.

The present authors[9] have applied a similar approach to study the viscosity of a blast furnace type slag containing 20 wt% Al_2O_3, 28 wt% CaO, 10 wt% MgO, and 42 wt% SiO_2, saturated with $MgAl_2O_4$ spinel particles at 1373°C. The composition of the slag was chosen so that it would be saturated by the spinel at or near the experimental temperature, thus minimising variations in the *melt* composition when $MgAl_2O_4$ was added. The viscosity was then measured after known additions of solid spinel particles.

The general consensus from these studies is that for slag/solid mixtures, the viscosity increases as the volume fraction of solids increases, and the mixtures follow a Bingham model[10] of liquid behaviour. Theories predicting the shape of lava flows assuming Bingham behaviour* of the liquid/solid mixture agree with observations in the natural world[11]. These studies have also shown that the Einstein-Roscoe type equations[12-15] describes the viscosity of high temperature two-phase systems adequately, that is:

$$h = h_0(1 - af)^{-n} \qquad (1)$$

where; h and h_0 are the viscosity of the solid containing and the solid-free melt respectively, f is the volume fraction of solid particles in the melt and a and n are constants.

The reciprocal value of a represents the maximum amount of solid that the melt could accommodate before the viscosity becomes “infinite”. For spherical particles of a uniform size, Roscoe suggested a and n to be 1.35 and 2.5 respectively[13]. Studies have found that using a = 1.35, and n= 2.5 gives a good representation to their data[7-9] but the best fit was obtained by allowing the parameters a and n to vary.

Metallurgical slags of practical interest such as fayalite and calcium ferrite type slags[16] are generally more fluid than the glassy blast furnace type slag studied previously[9]. This paper describes some of the work extending the technique developed for Al_2O_3-CaO-MgO-SiO_2 slags to calcium ferrite saturated with magnetite, another type of spinel. The aim was to determine if the flow behaviour was Newtonian, and to establish how the viscosity varied with the concentration of solid particles present in the liquid slag.

EXPERIMENTAL

The composition of the slag used in this work are presented in Table 1. The slag chemistries were selected so that both slags could be saturated with a solid spinel phase in air. The calcium ferrite slag was saturated with magnetite at 1225°C [17] whereas the blast furnace type slag was saturated with $MgAl_2O_4$ around 1375°C [16] in air. The calcium ferrite master slag was prepared by mixing powders of dried analytical or reagent grade $CaCO_3$ and Fe_2O_3. One hundred grams of the powder mixture was put into a Pt-13 % Rh crucible (about 100 cm^3 capacity) and then into the muffle furnace and melted at 1350°C. Once the slag was molten, additional powder was added to the melt (5 g at a time) and allowed to fuse and homogenise. When nearly full, the crucible was removed from the furnace and the slag poured into an inclined steel launder to quench. The above procedure was repeated until eight hundred grams of slag was prepared. All pieces of the quenched slag were combined and crushed and then the slag was remelted, quenched and crushed to a particle size of less than 10 mm for use in viscosity measurements.

Magnetite was prepared by melting reagent grade Fe_2O_3 in a Pt-13%Rh crucible at 1650°C and allowing to equilibrate for 2 hours before pouring onto a steel plate. The magnetite was then crushed in a rotary mill and screened to recover 3 ranges of particle sizes given in Table 2. The $MgAl_2O_4$ size fraction used in the previous study is also given in Table 2. The crushed magnetite was then dried at 105°C, sealed in a jar and placed in a desiccator for later use. For the calculation of particle volume fraction in slag, the density of the blast furnace type slag melt was taken to be 2.65 g cm^{-3} [16] and the density of the $MgAl_2O_4$ particles was estimated to be 2.88 g cm^{-3}. There is some disagreement in the literature on density of both the calcium ferrite slag and liquid iron oxide from which the magnetite was prepared. The data of Hara *et al.*[18] was used for both the slag and

* The rate of shear is directly proportional to the shear stress in excess of the yield value.

the magnetite to keep the work self consistent with the values being 3.85 g cm^{-3} and 4.40 g cm^{-3} respectively.

The experimental apparatus for the determination of viscosity of molten slags is shown in Figure 1. The slag was heated in a $MoSi_2$ element muffle furnace with a 250 mm x 250 mm x 250 mm chamber. The slag samples were contained in a Pt-13 % Rh crucible (55 mm average diameter, 47 mm high with slight taper) seated on a refractory brick and positioned directly under a vent tube through the roof of the furnace chamber. Measurements of the furnace temperature during viscosity heats were made with a Pt-6 % Rh/Pt-30 % Rh thermocouple inserted through the back wall of the furnace. The actual melt temperature was measured by lowering a sheathed Pt/Pt-13 % Rh thermocouple down the vent tube to the position of the crucible and was found to be about 20^{o}C higher than readings from the control thermocouple. The appropriate temperature corrections were then made accordingly.

A Brookfield DVII+ viscometer was connected by loops to a platinum extension rod (270 mm long, 2 mm diameter) and to a measuring spindle made of Pt-13 % Rh alloy. Two spindles were used, both had shafts 100 mm long and 3 mm diameter, and for the blast furnace type slag, the section of the spindle immersed in the melt had a diameter of 11.76 mm and a height of 25.15 mm. A larger 25 mm diameter spindle with a 25 mm height was used for the calcium ferrite slag. The viscometer spindles were calibrated against Brookfield standard oils, of known viscosity at 298 K in the range of 0.0493 to 30.8 Pa s. The spindle constant for each spindle was determined by measuring the torque at several rotation speeds at immersion depths (measured to the top surface of the spindle) of 5, 10, 15 and 20 mm. The viscometer was also validated at high temperature with the SRM slag supplied by Hoogovens RL. The agreement between the measured viscosities and the recommended values were well within the quoted experimental uncertainties[19].

The Brookfield viscometer was positioned over the muffle furnace vent hole, and crucible and spindle positioned in the muffle furnace. The spindle was suspended from the viscometer with a 7 mm spacing above the crucible bottom. After confirming that the spindle was able to spin freely, about 180 g of crushed slag was charged in the crucible. The furnace door was then closed and the furnace heated to temperature. For each melt the temperature dependence of the viscosity was measured before setting the temperature to 1280°C for the calcium ferrite slags and 1373°C for the blast furnace type slag to examine the effect of solid particles.

During the viscosity measurement, the particles were added by opening the furnace door and tipping approximately 0.5 g of the solid into the melt from a Pt crucible. The particles were stirred in by setting the viscometer to the highest rotation speed (60 or 100 rpm). The procedure usually took 20 to 40 seconds and the temperature loss during this time was allowed to recover in 30 minutes before the rotation speed was reduced back to the measuring range. This process was repeated to achieve required levels of solid addition. Measurements were conducted by logging the torque at a series of rotation speeds, taking 30-100 readings at each speed over 5 minutes.

At the completion of the experiment, the viscometer spindle was unhooked and the melt/spinel mixture poured out in the steel launder to form a string. Slag pieces were cut from the glassy strings for the preparation of polished samples of cross-sectional area of 200 mm^2. The condition of the crucible and the spindle was examined, but in all cases no solid particles were found to adhere to the spindle or the crucible wall.

RESULTS

The temperature dependence of the calcium ferrite slag and Al_2O_3-CaO-MgO-SiO_2 slag is shown in Figure 2. The viscosity of the solid-free calcium ferrite slag was at 0.065 Pa s at 1280°C, and the viscosity of the blast furnace type slag was 2.4 Pa s at 1373^oC. These values are in good accord with the extensive results from previous studies on these slags[16].

Figure 3 presents the measured viscometer torque reading for slags with addition of medium sized magnetite particles (0.3-0.42 mm) as a function of the spindle rotation speed. Within experimental scatter, the torque response may be reasonably well represented by a linear dependence on rotation speed. The viscosity was calculated from these results and is plotted versus rotation speed in Figure 4. The results show that the viscosity generally increases with the addition of solids. The apparent viscosity for melts containing fine (0.1-0.21 mm) and coarse (0.42-0.59 mm) magnetite particles are shown in Figures 5 and 6 respectively.

The viscosity of the calcium ferrite slag containing approximately 5 volume percent magnetite particles was between 3 and 10 times that of the solid free melt, and decreased as the rotation speed or shear rate increased. This dependence on shear rate became more evident as the volume fraction of solids increased. As the volume fraction of solids increased, the useable range of rotation speed became smaller, the rotation speeds were slower and the measured viscosity became increasingly dependent on the rotation speed. The limit to the concentration that could be studied was then the available speeds where the viscometer was not over range. Extrapolating the torque measurements in Figure 3 to zero rotation speed suggests a small residual torque which was more apparent with increasing solid loading. This trend was evident for all the particle sizes studied.

The mean values of the viscosity are plotted in Figure 7 versus the amount of solid addition for the three groupings of particle size experiments with calcium ferrite slag. Also shown is the results from a repeat experiment with the medium sized particles. The mean viscosity values were obtained by taking an average of the viscosity shown in Figures 4, 5 and 6 over the rotation speed range. As described above, the viscosity increased with the addition of the solid magnetite particles. The increase is initially slight but becomes more marked at higher levels of solid loading. Figure 7 also shows that for the same level of solid addition, bigger sized particles generally tend to have a more significant effect on the viscosity of the slag.

Figure 8 shows a polished section of a slag sample with the medium sized magnetite particles dispersed in the slag matrix. The present work was intended to maintain the composition of the slags saturated by the solid particles. In practice, slight deviation from the conditions for saturation could lead to precipitation or dissolution of the solid spinel. No systematic confirmation of the solid level in the melt was made. However, a few solid particles were seen to float on the surface of the molten slag after viscosity measurements were made even for the initial addition of only 1 g of particles to the slag.

DISCUSSION

There is general consensus that the rheological properties of geological silicate melts deviate away from Newtonian behaviour when the melt contains solid particles[8] and metallurgical slags are expected to behave similarly[15]. When the Al_2O_3-CaO-MgO-SiO_2 slag was saturated with $MgAl_2O_4$ particles, it was observed[9] that the relationship between the measured torque and the rotation speed deviated from Newtonian behaviour to that observed for liquids that shear thin or are Bingham[10] in nature. This deviation suggests that there may be a residual shear stress for the liquid-solid mixture although there is some debate about this. Kerr and Lister[20] argue the true rheology of a silicate containing solids is shear thinning with a Newtonian limit at small shear rates and that the yield stress is an artefact of extrapolation to zero shear rate.

Figure 3 shows that the behaviour of the calcium ferrite melt containing solid particles deviate away from Newtonian behaviour as the volume fraction of solids increases. Figures 4, 5 and 6 show that the viscosity decreases as the rotation speed increases, ie, shear thins or follows Bingham type behaviour similar to the study on the Al_2O_3-CaO-MgO-SiO_2 slag saturated with $MgAl_2O_4$ spinel particles[9]. The magnitude and trends of the residual shear stress for the calcium ferrite slags is similar to that observed previously [9], indicating that the apparent non-Newtonian behaviour is due to the *solid-melt suspension* rather than to experimental error.

The study by Sältzer and Schulz[1] on the viscosity of a molten salt containing glass particles suggest that there is a limiting value for the viscosity as shear rate increases. In their study, the viscosity decreased as the shear rate increases and flattened to a limiting "true" viscosity at shear rates above 20 and 30 s^{-1}. The maximum shear rate of this study used was 36 s^{-1}, but at the lower shear rates, it is very likely that the shear rates were not great enough to measure the "true" viscosity. Therefore greater weighing should be placed on the data collected at the higher shear rates or lower solids content.

Figure 9 shows the relative viscosity calculated from the average viscosity data shown in Figure 7. Also shown in Figure 9 are the relative viscosities from the study on the Al_2O_3-CaO-MgO-SiO_2 slag and spinel. Both slag types show the same trends, even though the viscosity of the pure liquid ferrite slag is nearly 40 times lower than the silicate slag. The scatter in the results increased as the solids content increased, probably reflecting the errors due averaging the viscosity which is varying with the shear rate. The influence of the volume fraction of solids for the calcium ferrite slag on the viscosity seems to be greater than that of the silicate.

The Einstein-Roscoe equation (Eq 1) has been shown to adequately describe the viscosity of silicates. Lejeune and Richet[8] found that with $n=2.5$ and $a=1.35$, equation 1 was found to describe the viscosity of a silicate glass reasonably well, but the best fit was obtained by allowing both parameters to vary. A similar result was found the Al_2O_3-CaO-MgO-SiO_2 slag and spinel particles[9], although a single parameter fit, allowing a to vary and fixing n=2.5 also gave a good fit to the data. The results of the previous study suggest that there may be some dependence of a and n on the particle size. The viscosity data in this study are too few in number and influenced by shear rate at the higher solids concentration to evaluate the dependence on particle size. The lines of best fit to the calcium ferrite slag and the silicate slag are also shown in Figure 9. The fits were determined placing greater emphasis on the data where the solids content was less than 7 volume percent. The values of a were 4.4 and 3.2 for the ferrite and silicate slag respectively.

It is thought one of the factors that may also influence the viscosity is the shape of the particles. There have been plenty of studies indicating that shape can influence the rheological properties of mixtures and theories have been developed to take into account the particle shape[1]. The particles used in this study have come from the spinel family and although are prepared in very different manner, the particles had similar shape and behaved similarly in the slags studied. It also appears that spinel crystals in slags have a much greater influence on the slag viscosity than expected for spherical particles. The theoretical value of a in the Einstein-Roscoe equation is 1.35, and the fitted value for the calcium ferrite slag is 4.4 and between 2.6 and 3.4 for the Al_2O_3-CaO-MgO-SiO_2 slag depending upon the spinel particle size[9]. It would be worthwhile however employing the approach developed in this study using a viscometer that can measure at much higher shear rates. It is likely that the value of the a parameter may tend towards the theoretical value.

This is one of the first studies investigating the effect of solid particles in a slag of interest to metallurgical processing. The trends observed here are consistent with observations from other studies where the behaviour of slags containing solid particles was implied. From the results of this study, an estimate of the effect of solid particles could be transferred to other systems of metallurgical interest to estimate the effect on the viscosity. When combined with both viscosity models for liquid slags and thermodynamic models predicting the composition and mass of liquid and solid phases, the data could be useful in determining if a slag can be tapped from a furnace.

CONCLUSIONS

The viscosity of a calcium ferrite slag at 1280°C was determined with the addition of magnetite particles. The slag/magnetite mixture showed apparent Bingham behaviour consistent with observations of Al_2O_3-CaO-MgO-SiO_2 slags saturated with spinel particles.

The dependence of the viscosity on the amount of solid addition could be described by the Einstein-Roscoe type equation

$$h = h_0(1 - af)^{-n}$$

The effect of solids in the slags appeared to be much greater than expected from theory. Fitting of the data with *n* fixed at 2.5, yielded a value of 4.4, significantly higher than the theoretical value of 1.35 for uniform spheres.

The effect of solid particles in calcium ferrite slags seems to be greater than calcium alumino-silicate slag although effect of the shear thinning on the viscosity may be influencing the magnitude of the viscosity dependence. It would be worthwhile extending the measurements to higher shear rates.

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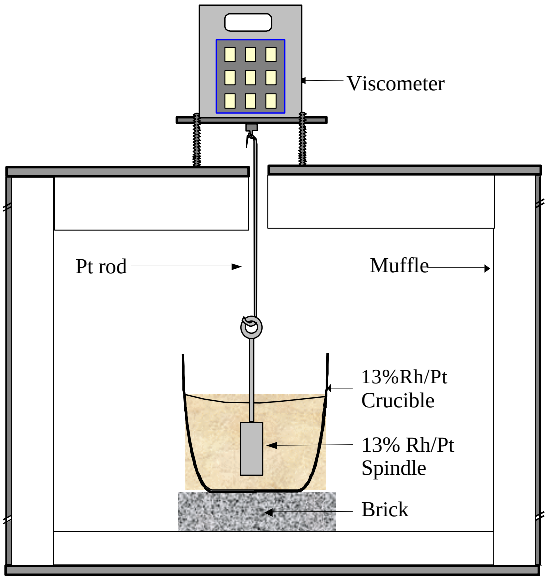

Figure 1: Schematic drawing of the experimental apparatus. (Not to scale)

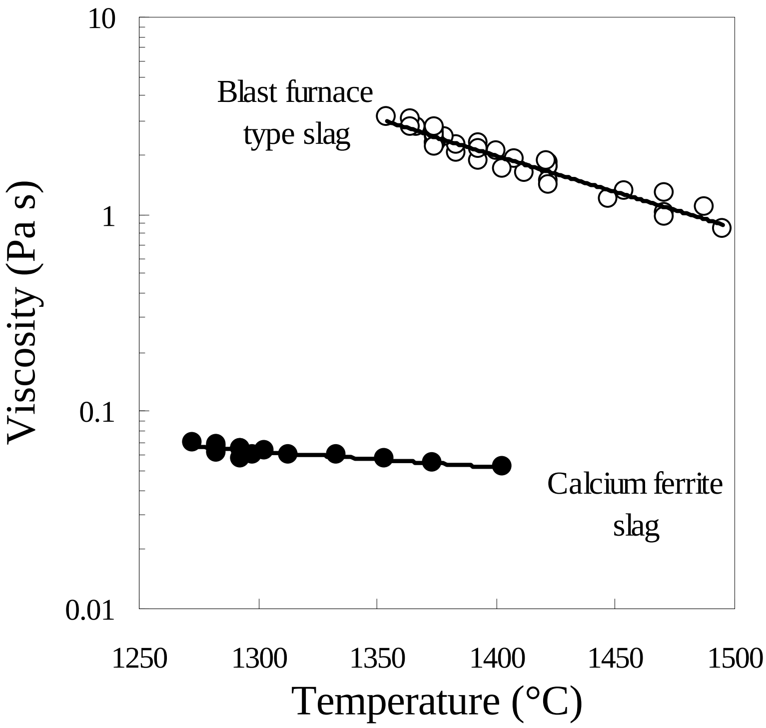

Figure 2: Temperature dependence of the homogeneous liquid viscosity of the Blast furnace and Calcium ferrite slags used in this study.

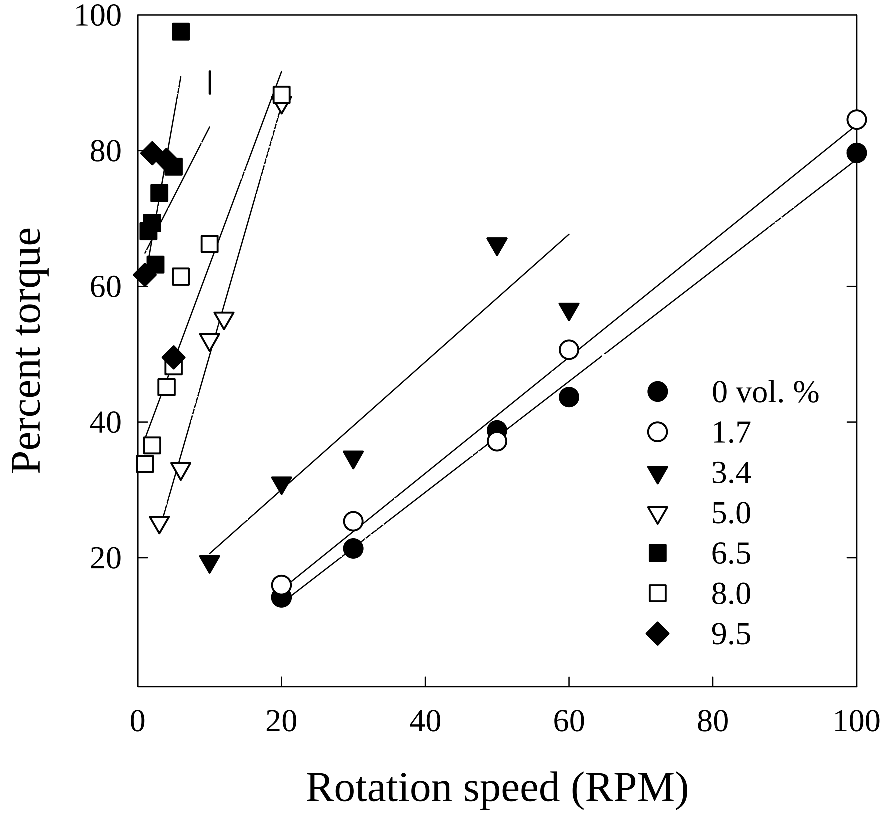

Figure 3: Measured percentage torque versus the rotation speed for the calcium ferrite slag with medium (0.3-0.42 mm) magnetite particles.

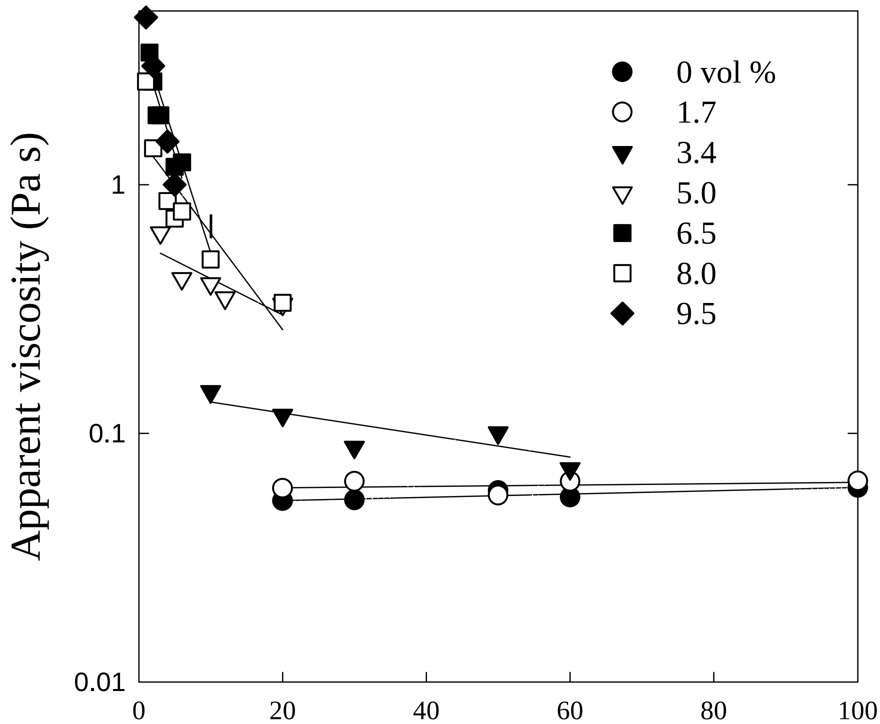

Figure 4: Apparent viscosity versus the rotation speed for the ferrite slag with medium (0.3-0.42 mm) magnetite particles.

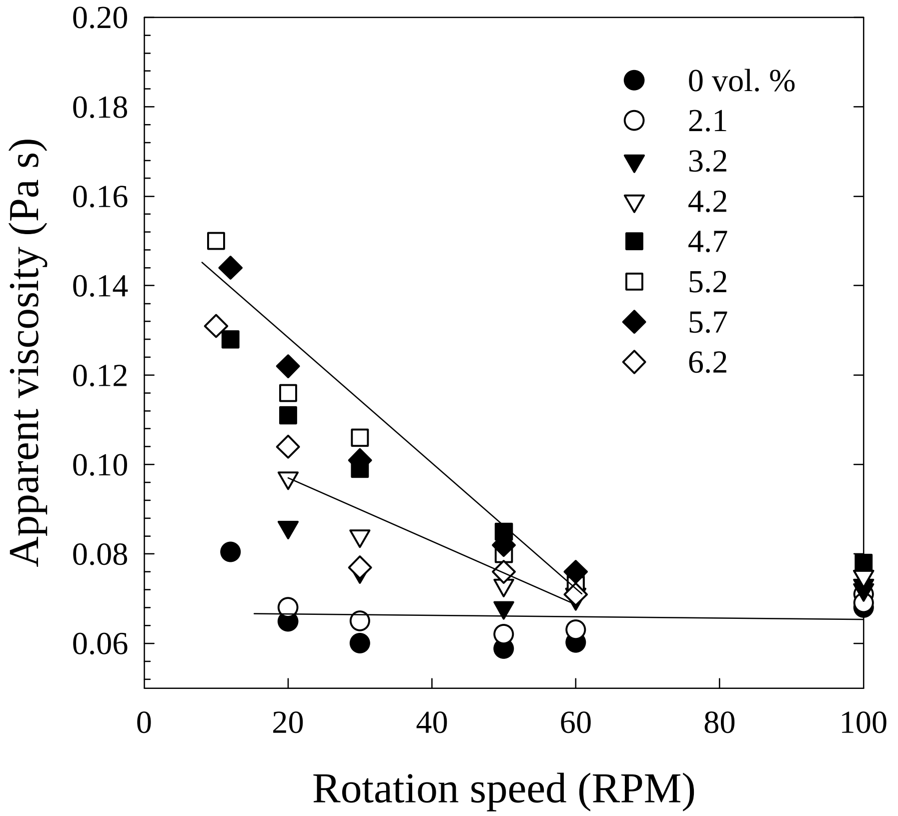

Figure 5: Apparent viscosity versus the rotation speed for the ferrite slag containing fine (0.1-0.21 mm) magnetite particles.

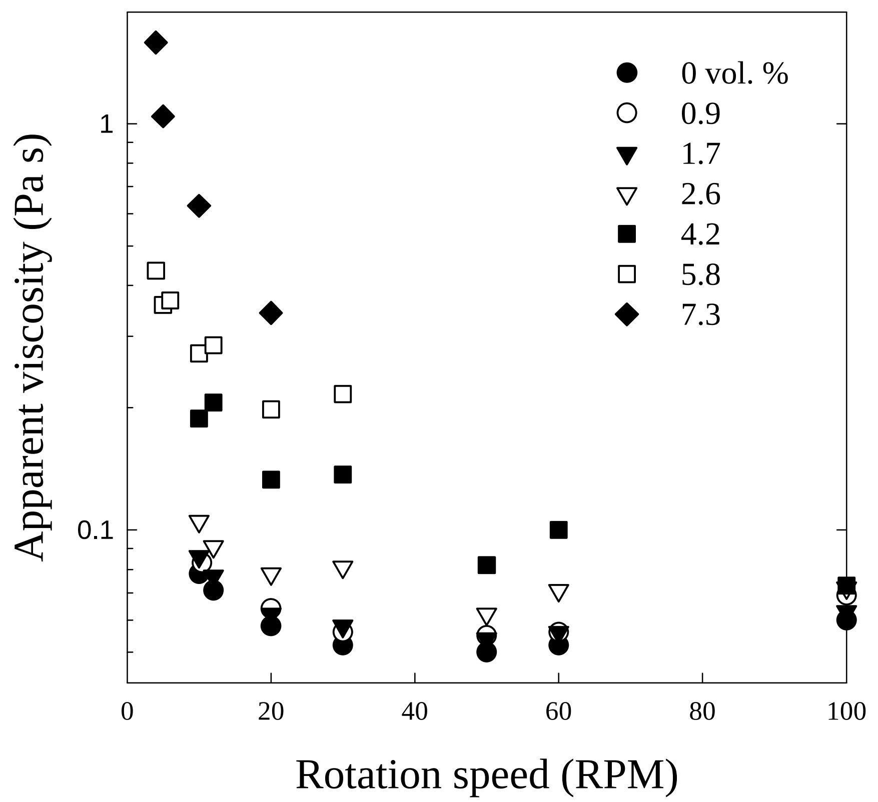

Figure 6: Apparent viscosity versus the rotation speed for the ferrite slag containing coarse (0.42-0.59 mm) magnetite particles.

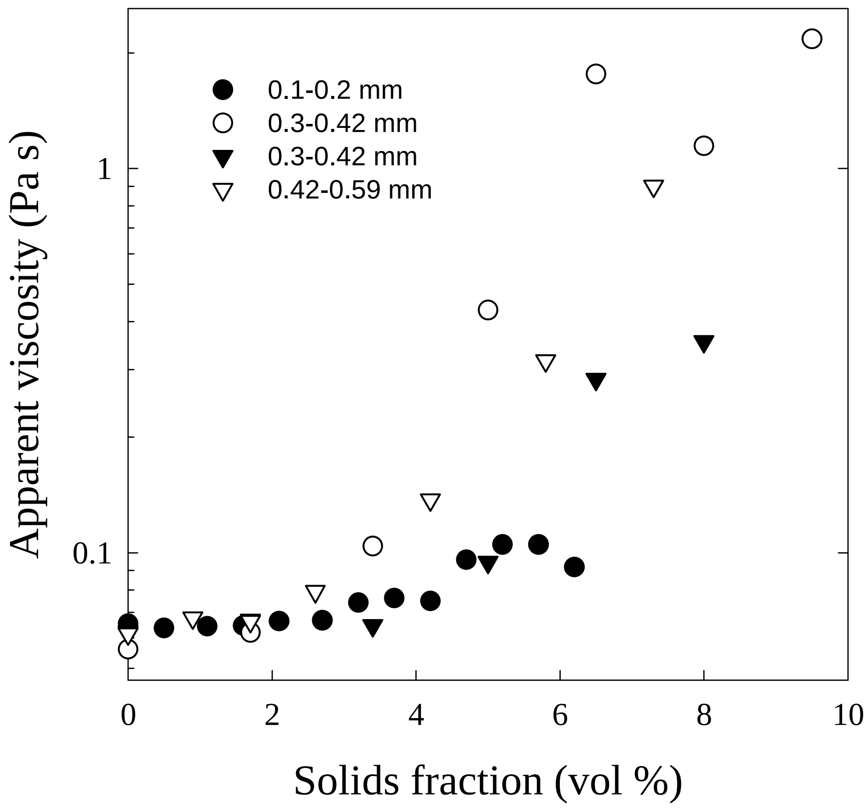

Figure 7: The average viscosity of the calcium ferrite slag plotted as a function of the magnetite content.

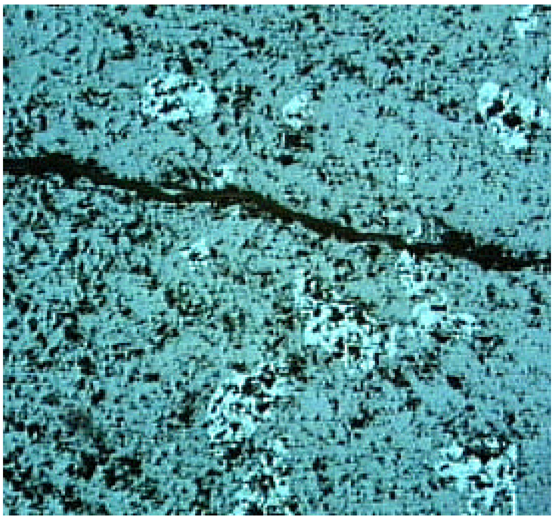

Figure 8: Polished optical section showing magnetite crystals dispersed in the quenched ferrite slag.

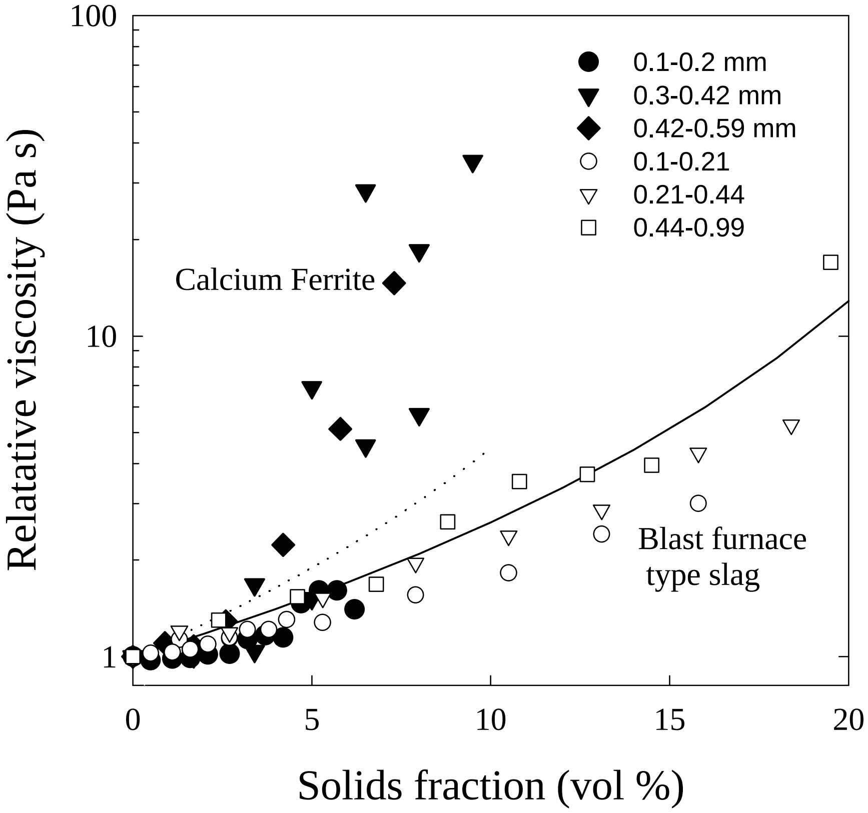

Figure 9: Relative viscosity (η/η_o) as a function of solids content for calcium ferrite melts containing magnetite particles (closed symbols) and Al_2O_3-CaO-MgO-SiO_2 slag containing $MgAl_2O_4$ particles (open symbols). The lines are the best fit to each slag/solid mixture according to the Einstein-Roscoe equation with *n* =2.5.

Table 1. Composition of the slags in this study

Component	Calcium ferrite slag (wt %)	Blast furnace type slag (wt %)
Al_2O_3		20
CaO	19	28
FeO_x	81	
MgO		10
SiO_2		42

Table 2. Fe_3O_4 and $MgAl_2O_4$ particle sizes in this study

Designation	Fe_3O_4	$MgAl_2O_4$
Fine	0.10 to 0.21 mm	0.10 to 0.21 mm
Medium	0.30 to 0.42 mm	0.21 to 0.44 mm
Coarse	0.42 to 0.59 mm	0.44 to 0.99 mm