DRAINAGE OF MOLTEN CaO-SiO_2 - Al_2O_3 SLAG FILMS

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ABSTRACT

A gravimetric technique has been developed for the measurement of the draining rate, average thickness and rupture time of molten slag films. Results for liquid films withdrawn from CaO-SiO_2-Al_2O_3 slags at temperatures between 1300-1500 °C are presented. The addition of P_2O_5 as a surfactant, and the effect of basicity on the film draining rate will be discussed. A laser interferometric technique used as a method of measuring the thickness profile of draining films will be presented. Results for the withdrawal of slag films on a thin platinum plate are also shown, and comparisons made with those withdrawn on wire frames. Possible stability mechanisms, and their influence on slag film drainage are discussed.

1. INTRODUCTION

Foaming slags are critical features of new iron-making processes. Slag foams provide a large gas-slag contact area for multiphase reactions to occur, act as a medium for heat-transfer to the bath from the post-combustion of CO, and protect the roof refractories from excessively high temperatures.

Slag foaming has attracted the attention of a number of researchers who attempted to establish the behavior of slag foams using the "inert gas injection technique," originally developed by Bikerman[1] for aqueous foams. This involves injection of an inert gas into a molten slag at a constant gas flow rate. The height of the foam column attained at a standardized gas flowrate is defined as the *foamability*. The decay rate of the foam column when gas injection is ceased is then used to define the *foam stability* or *foam life*.

Using the inert gas injection technique, Cooper and Kitchener[2] measured the time required for the decay of a foam column from an arbitrary steady state height, in the temperature range 1350-1700 °C. No stable foam was observed for a CaO-SiO_2 system, however, small additions of P_2O_5 markedly increased the foam life. They concluded that the stability of foams formed during steelmaking was not primarily dependent on viscosity, and that dilute solutions of surface active solutes could create the necessary surface elasticity (resistance to stretching) to stabilize the foam film and therefore the foam. This is due in part to the depletion of the solute concentration in the bubble films, and to the difference between the dynamic and static surface tensions of the films, according to these authors.

Swisher and McCabe[3] used the same type of apparatus for the measurement of foam life for a CaO-SiO_2-Cr_2O_3 slag at 1600 °C, and suggested the Marangoni[4] effect to be the most significant contributor to foam stability. Hara and Ogino[5] studied the CaO-SiO_2-FeO slag system from 1250-1300 °C and suggested a decrease in slag surface tension was responsible for the observed increase in foam life, when the O/Si ratio was decreased. Kozakevitch[6] postulated that stabilization was due to electrical double-layers consisting of adsorbed structural units (eg PO_4^{3-}), where repulsion between the charged layers opposes thinning and approaching of gas bubbles.

Ito and Fruehan[7] stated that the approach taken by Cooper and Kitchener[2], Swisher and McCabe[3] and Hara et al[5] involved a defined foam life which was totally arbitrary. It did not allow for the prediction of foam heights in practical processes. Ito and Fruehan studied the foaming of a CaO-SiO_2-FeO system for temperatures up to 1400 °C. A foam index (Σ) was used to describe the foamability of the slag, with an electrical probe technique being used for the measurement of steady state slag foam height. An empirical equation was derived to relate the foam index to the physical properties of the slag, and this information used to predict the likeliness of foaming in practical metallurgical processes.

The stability of aqueous foams (e.g. usually those containing sodium dodecylsulphate as a surfactant) has been studied in great detail over the years[1]. Single foam films have been a source of great interest, as they are the simplest model of a foam unit and thus allow the study of the forces of interaction operating within a foam. Investigation of foam stability has generally involved the measurement of the soap film thickness and its draining rate before rupture, as the mechanisms of stability relate directly to these factors. The thickness of a typical soap film can range from a few microns down to tens of angstroms (if the environmental constraints are suitable). Both the Gibbs elasticity and Marangoni effect are thought to be important stabilizing factors and it has also been acknowledged[8] that Van der Waal's forces (or electrical double layer interactions) begin to operate when the films are generally < 0.1 μm thick.

Aqueous foam films have been previously classified[8] according to characteristic "modes" of draining. For instance, "rigid" films are classified as those having immobile (compacted) surfaces which generally show slow draining rates. On the contrary, "mobile" films have moving surfaces, with lower surface viscosities, and thus their draining rates are usually faster than rigid films. The draining is often dominated by mechanisms like the Marangoni effect (induced by surface tension gradients). These films have free surface flows which are often visible as a "thinning action" in and around the film borders. Molten slag foams, when well drained, consist of a network of films joined at the Plateau[9] border regions. A knowledge of the thickness profile of slag films can yield interesting information regarding their draining characteristics. The film can thin uniformly or non-uniformly, depending on the type of stability mechanism(s) operating.

Despite all the effort in studies of slag foaming, the basic characteristics of the foam films are still poorly understood. There is no clear knowledge of the typical film thickness and the draining rate of slag foam films. The present work was aimed at measuring/estimating the thickness of foam films and characterizing the draining behaviour of foam films of molten CaO-SiO_2-Al_2O_3 slags.

2. EXPERIMENTS

2.1 Gravimetric draining experiments on free liquid films

A gravimetric technique was used for the measurement of the *average* thickness and the draining rate of "free" (wire frame) films. The apparatus is shown in Figure 1. Heating of the sample was by a $MoSi_2$ muffle furnace, capable of temperatures up to 1700 °C.

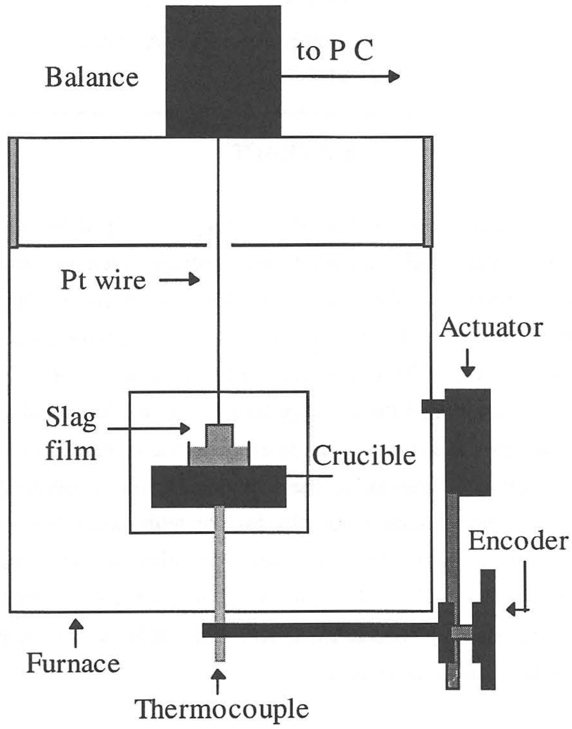

Fig.1. Gravimetric apparatus for measurement of film thickness and draining rate of slag films.

Measurement of the *average* slag film thickness and draining rate was by suspension of a 0.35 mm diameter Pt/Rh rectangular wire frame from an electronic balance (Sartorius R200D, sensitivity up to 0.1 mg), which was connected to a 486 PC equipped with a data logging program. Sample temperature was recorded using a Pt/Pt-13%Rh (Type R) thermocouple enclosed in an alumina sheath, the end of which was attached to a cast ceramic pedestal, securing a Pt/Rh crucible, (40 mm, outer diameter and 40 mm height) containing the slag sample. The crucible and its content could be moved up or down within the furnace hot zone, using a linear motion actuator. During each experiment, the sample was initially melted and maintained at the experimental temperature for about 30 minutes, with the wire frame suspended immediately above the slag surface. To begin a measurement, the crucible was slowly raised until the slag surface contacted the wire frame, indicated by the sudden change in readings on the numerical display of the balance.

From this point, the sample was raised until the bottom section of the wire frame was immersed to a depth of 5 mm. Balance readings were then logged for a period of about two minutes and the variation was typically within ±(1-2) mg. The average of this mass constitutes that of the wire frame with no film present (M_o). The sample was then raised further until the wire frame was immersed completely in the slag. The crucible was then lowered a predetermined distance at a speed of 50 mm/s and a distance resolution of 0.1 mm as indicated by a linear encoder attached to the actuator. A draining thin film was then partially withdrawn on the wire frame, the bottom section of the frame remaining immersed at the depth of 5 mm.

As the film drains, its change in mass was recorded as a function of time. The net mass of the film was obtained by subtracting M_o and correcting for the pull due to surface tension. The value for the surface tension was from the measurements by Mukai.[10] The average thickness of a film was then calculated with a knowledge of the film area and the density of the slag.

2.2 Sample Preparation

Slag samples were prepared using AR grade SiO_2, Al_2O_3 and $CaCO_3$ dried powders as the starting materials. Additions of P_2O_5 were made in the form of dried orthophosphate powder, $CaH(PO_4)_3.2H_2O$. Samples were well mixed and premelted in a Pt-Rh crucible in a muffle furnace at 1550 °C in air. The solidified glassy samples were pulverized using a WC_2 ring-mill and then remelted in air to ensure homogeneity. The samples were ready to use after quenching on a copper plate in air and followed by pulverization. CaO-SiO_2-Al_2O_3 slag samples were thus synthesized with CaO/SiO_2 ratios ranging from 0.51 to 1.20. The effect of small additions (< 2 wt %) of P_2O_5 on the film thickness and draining rate was studied for CaO/SiO_2 ratios of 0.70.

2.3 Laser Interferometry Experiments

The film draining experiments were also recorded using a color CCD video camera to observe any intrinsic thinning features, such as those generally observed with soap films i.e., color interference patterns and movement of liquid on the film surface or around the Plateau borders. A laser interferometer was also constructed to measure the thickness profiles of the draining films at high temperatures.

A schematic of the laser interferometry experiment is shown in Figure 2. The interferometer consisted of an argon-ion laser source operating at 488 nm, a cubic beamsplitter (BS), and two mirrors, M_4 and M_5 (mirrors M_1-M_3 served to direct the beam to BS around an optical tabletop). The beamsplitter divided the laser into two parts (of equal intensity), one being transmitted through optical quality silica windows (W) through the furnace hot zone toward mirror M_4, the other part being reflected toward mirror M_5. The two mirrors, M_4 and M_5, returned the beam to BS. There the beams recombine, and interference was observed at BS through an optics train and the CCD video camera. One of the mirrors (M_5) is mounted so that it can be moved along its axis, to equalize the two pathlengths.

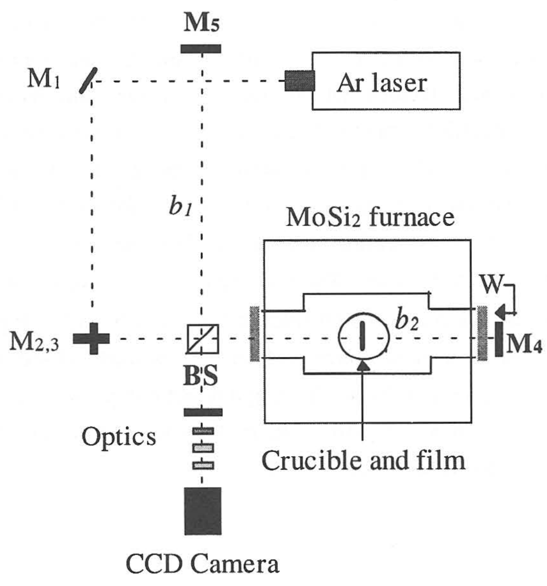

Fig.2. High temperature laser interferometer.

In the absence of a thin film, the path difference for the two beams when they recombine is $2b_2$ - $2b_1$ and the image recorded is called the "zeroth order fringe pattern." Any change in path length introduced by the presence of a thinning film, will cause a change in the relative phase of the two beams as they recombine. Thus if the thickness of the film changes by $\lambda/2$, the path difference changes by λ and thus the fringe pattern will shift by one fringe.

When a film is formed and immediately begins thinning, the number of fringes appearing in and out of the field of view are counted. Each visible fringe has a known wavelength of 488 nm, and the total number counted before rupture is thus the relative change in thickness due to film thinning. The entire wire frame is illuminated by the beam and it is possible to deduce the location of any thinning spots within the film.

2.4 Slag film drainage from a platinum plate

A series of gravimetric film draining experiments were also carried out using a thin platinum plate as a solid substrate. The draining of the "plate" films would be expected to be different to the "free" liquid (wire frame) films discussed earlier, as the former do not possess a Plateau border region, and the effects of surface tension are negligable.

The experiments involved the partial withdrawal of a thin platinum plate (25 mm x 10 mm x 0.28 mm) from the molten slag to a fixed height of 14 mm. A liquid film was immediately formed, which drained with time, and its mass was recorded gravimetrically, as shown schematically in Figure 3. The film withdrawal speed and thickness calculations were analogous to those used for the free films, however a correction for the surface tension was not required in this case. The recorded net mass corresponded to identical films on both sides of the plate, as seen in Figure 3. The area of the films (1.4 cm^2), was made identical to those of the free films, allowing a direct comparison of their draining behavior. An average thickness of a film was calculated from the recorded mass.

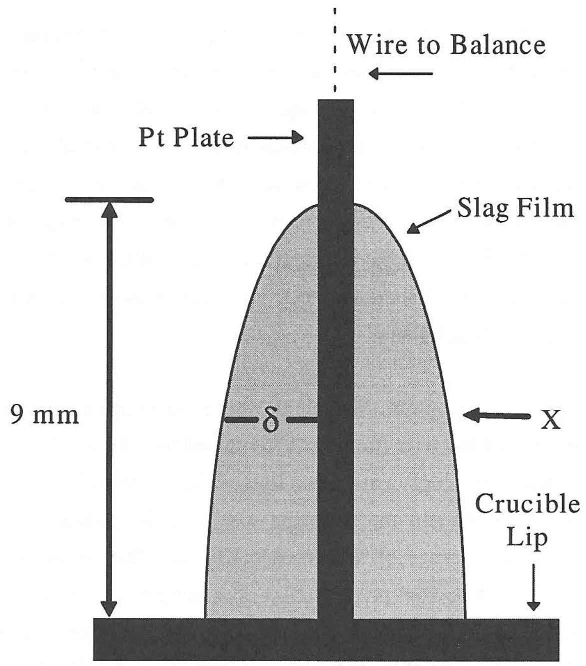

Fig.3. Gravimetric and video profiling thickness measurements using a thin platinum plate.

Directly observing the draining of films on solid substrates offers advantages if one is attempting to obtain further quantitative data, such as the thickness profile and change in thickness during the initial stages of slag film drainage. Attempts were made to observe and thus measure the above quantities for the plate films, through the use of an image analysis technique.

The starting film thickness and the thickness change during the initial draining stage was measured by video imaging an enlarged side view of the plate experiments, as depicted in Figure 3. When reviewing the recorded draining film on videotape, a thickness change in the parabolic profiles could be made, frame-by-frame, from a fixed position (X). Using image analysis software, a line calibration (in pixels) was first made for the thickness of the platinum plate from the video image, and thus any subsequent film thickness measurements could be compared to the calibrated thickness (first measured accurately using a vernier). For consistency, the total thickness across the films on either side of (and including) the plate were measured.

Analogous to the gravimetric plate film experiments, results presented are for thickness measurements involving a film on one side of the plate only.

3. RESULTS and DISCUSSION

3.1 Draining of "free" and "plate" slag films

A pair of typical "free" film draining curves obtained from the gravimetric technique are shown in Figure 4. The *average* film thickness is plotted on the Y-axis. Useful information obtained from such plots included the average film thickness before rupture (critical thickness) and rupture time. Both appear quite reproducible within a few seconds, irrespective of temperature.

As shown in Figure 4, the film thickness changes with time, but not in a smooth manner. An average rate of draining or thinning was obtained by a linear regression of the thickness versus time, 3 seconds after the start, to the point of rupture. Alternately, the rate was obtained by regressions of the mass versus time. The results for a melt containing 18 wt % Al_2O_3 with CaO/SiO_2 = 0.93 are shown in Figure 5, plotted as a function of temperature. The corresponding film life (or the rupture time) is also plotted in Figure 5. As can be readily observed, there exists a clear linear relationship between the reciprocal of temperature of the slag, the film draining rate and the film life. As expected, the film draining rate decreases with decreasing temperature, indicating that the flow within the liquid films becomes slower, with a concomitant increase in film life.

Calculation of the average film thickness accurately has proved more difficult, as the surface tension of the slag must be known. The literature values tend to vary among different authors and are generally quoted for temperatures greater than those used in this study. To prevent any distortion of the results, the "raw" data for the draining rates have been plotted i.e., the units shown are mass per unit time (g/s), rather than the usual cm/s.

The draining curve in Figure 4, shows that the starting film thickness is around 120 µm, with a critical thickness of around 30 µm before rupture. From these values, it would initially appear that these films are relatively thicker than those associated with typical aqueous films, which have been reported to start at around a few microns and thin down to hundreds of angstroms.[8] The uncertainty associated with the surface tension correction will thus have a great effect on the certainty of these values. It is highly probable that the films are thinner in their centre.

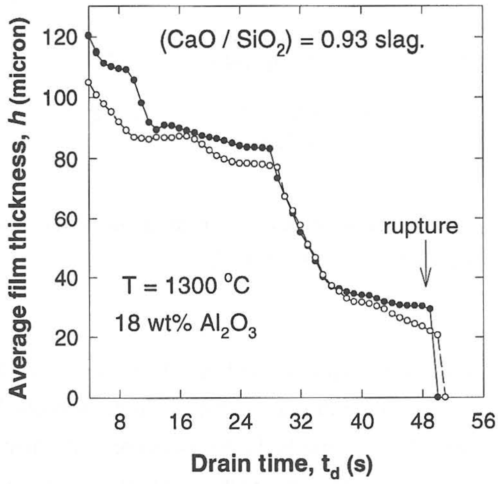

Fig. 4. Draining curve for an 18 wt % Al_2O_3-CaO-SiO_2 slag film at 1300 °C.

Another characteristic worthy of further investigation is the presence of "flatter" regions followed by steep "shoulders" in the draining curves (Figure 4). They could be due to an induced cooling effect on the film, possibly by a temperature gradient produced when the films are withdrawn from the melt surface, for instance the temperature of the slag has been measured to decrease one to two degrees Celcius after film withdrawal. However, such characteristics were less prominant when the draining curves were observed at higher temperatures. Another reason could be due to an intrinsic thinning behaviour within the film i.e., depending on the type of stability mechanisms operating, the thinning rate may increase, or decrease.

It has been reported elsewhere[11] that the lifetimes of aqueous films vary quite considerably between consecutive measurements on a chosen system. The general reason is uncertain, but it has been postulated to be due to a difficulty in reproducing the molecular structure of the film surfaces.

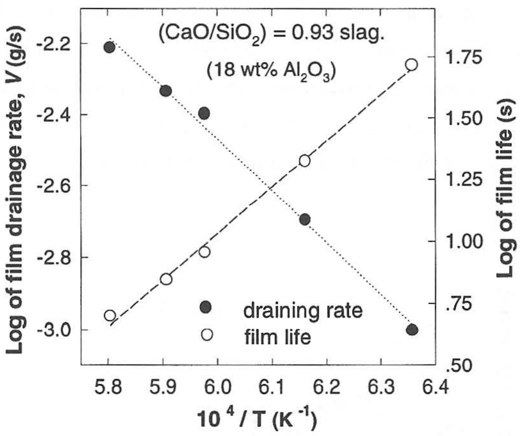

Fig.5. Temperature dependence of film draining rate and film life from 1300-1500 °C.

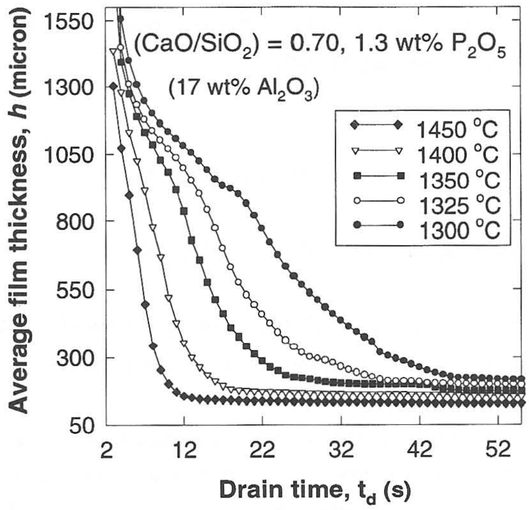

Fig.6. Slag film drainage from a thin platinum plate, with identical area to that of the free films.

It is rather encouraging to find that the present technique was able to record the film life or rupture time reproducibly. Film lifetimes were found to be temperature dependent, as seen in Figure 5, with the recorded rupture time usually identical for repeat experiments at a given temperature above 1300 °C (rupture times varied within 3 to 5 seconds of each other at around 1300 °C).

Typical results obtained from the gravimetric plate film draining experiments, are shown in Figure 6. The plate film area was made identical to that of the free films. The smooth curves obtained imply that uniform film draining occurs down the plate, with no "flat" or "shoulder" characteristics present, as were generally observed with the free films.

3.2 Effect of basicity on the draining of "free" films

The effect of CaO/SiO_2 ratio (basicity) on the film draining rate was expected to follow the general trend i.e., a lower basicity (higher viscosity) should result in a decrease in the draining rate. The effect of temperature and slag basicity on the film draining rate between 1300-1450 °C for slags with CaO/SiO_2 ratio of 0.51 to 1.20 respectively, is shown in Figure 7. For each slag, the draining rate shows a strong temperature dependence, as mentioned previously. At a given temperature, the rate was observed to decrease with increasing CaO/SiO_2 ratio within the range studied, i.e., from 0.51 to 1.20. This is rather surprising, as it shows a reverse of the trend expected if viscosity were to have a strong influence.

At the present, it is uncertain as to the validity of this trend, however a complex effect of viscosity on the draining rate has also been demonstrated previously by the authors,[12] in a model Na_2O-B_2O_3 system at temperatures up to 1000 °C.

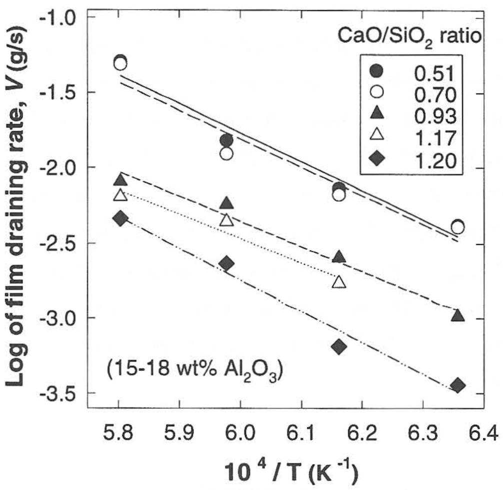

Fig.7. The film draining rate obtained at varying temperatures, plotted to show the effect of slag basicity.

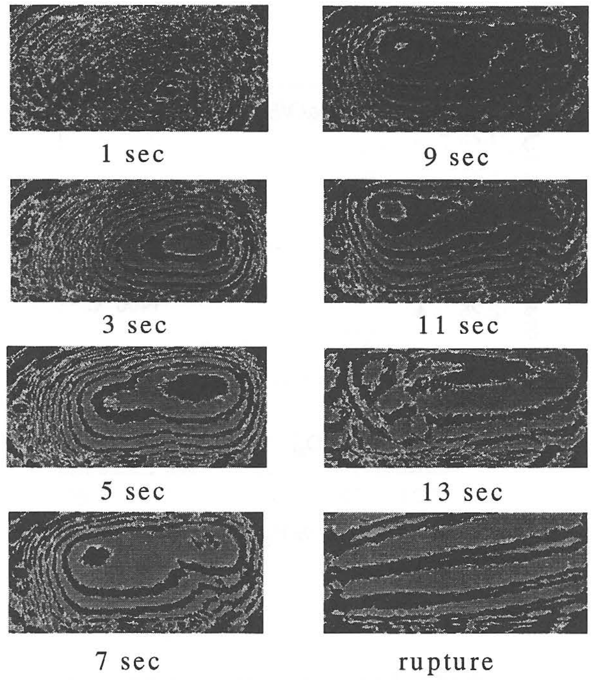

Fig.8. Interferograms showing thinning of a 15 wt % Al_2O_3-(CaO/SiO_2)=0.51 free film at 1420 °C.

3.3 Observations and free film thickness profile using laser interferometry

While observing and recording the draining behaviour of free films through the use of a color video camera, it became apparent that the cross-sections of these films were non-uniform. Arrays of colored bands were observed on these films. These color bands are analogous to those normally observed with typical soap films.

Laser interferometry[8] has been used to measure the thicknesses of aqueous films at room temperature, and was thus applied to draining slag films at temperatures up to 1450 °C. A series of the resulting interference patterns are shown in Figure 8, where a localized thinning spot is seen to appear very quickly and spread across the face of the film before rupturing. One can thus confirm, with a high degree of certainty, that these films in fact thin non-uniformly and exhibit behavior characteristic of "mobile" films which have free surface flows.

3.4 Effect of P_2O_5 as a surfactant on slag film drainage

The effect of surface tension on the stability of slag foams has been well documented,[2,3] with a lowering of the surface tension favorable for foaming. The effect of P_2O_5, a strong surfactant, on the draining rate of free films was investigated. The film draining rates in Figure 9 (a), obtained from this series of experiments between 1300 and 1450 °C are plotted. As shown by these results, the draining rate decreases with the addition of P_2O_5 at a given temperature. With the addition of 1.3 wt % P_2O_5, the rate dropped by a factor of about 2 at 1300 and 1350 °C. At the higher temperature of 1450 °C, the drop was by a factor of about 6. Despite the decrease in the draining rate, the rupture time of the slag film did not seem to change with P_2O_5, as shown in Figure 9 (b) for the slag (17 wt % Al_2O_3, CaO/SiO_2 = 0.70). at 1400 °C.

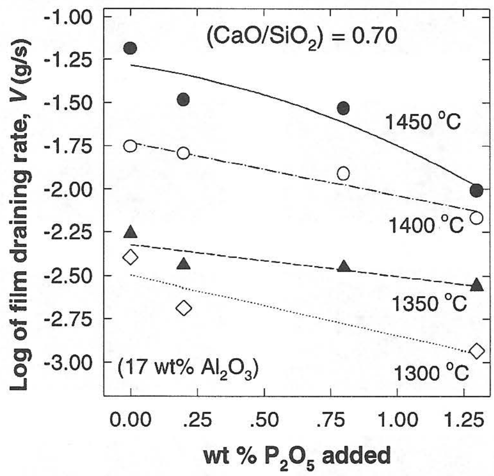

Fig.9 (a). Effect of P_2O_5 addition on the draining rates of free films at 1300 to 1450 °C, for slags of 17 wt% Al_2O_3 and $CaO/SiO_2 = 0.70$.

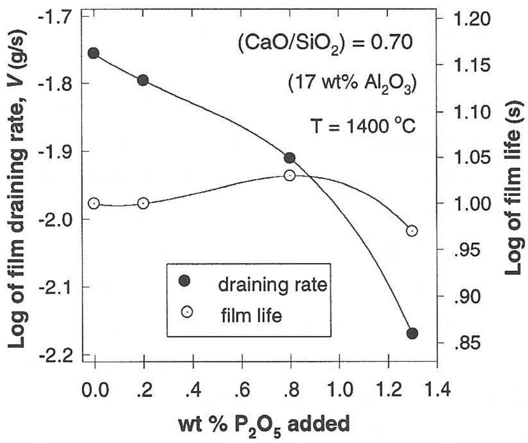

Fig.9 (b). Effect of P_2O_5 addition on the draining rate and life of free films at 1400 °C.

A lowering of the slag surface tension, induced by the adsorption of P_2O_5 may result in a lowering of the Plateau border suction force. This would lower the film draining rate, due to a concomitant decrease in the Laplace pressure[1] operating within the films viz., $P_{cap} = 2\gamma/r$; where γ is the surface tension of the melt (the factor 2 arises from the film having two surfaces), and r is the radius of curvature of the film, in the Plateau border region.

Rather than the absolute surface tension having an effect on foam film stability, it has been acknowledged[13] that the surface tension depression per unit concentration change of surfactant ($\Delta\gamma$/mol %), is a more important criterion when determining the inherent stability of a foaming slag system i.e., the larger the value of $\Delta\gamma$/mol %, the greater the stabilizing effect or "Marangoni elasticity." Slag systems containing P_2O_5 are more likely to have such an inherent elasticity and thus produce more stable (slower draining) foams.

3.5 Film drainage from a thin platinum plate

The curves from the gravimetric plate experiments in Figure 6 are very smooth, implying uniform drainage. The thickness profiles of the draining plate films was also recorded with a CCD camera, and confirmed the assumption that they are in fact parabolic during the early stages of draining, as has been depicted schematically in Figure 3. For parabolic profiles, one expects the film thickness δ at a known height x, after a draining time t_d, to follow an equation postulated by Jeffreys.[14]

$$\delta_{\mu m} = \left[\frac{\mu . x}{\rho . g . t_d} \right]^{1/2} \qquad [1]$$

where μ is the slag viscosity (Poisse), ρ is the slag density (g/cm^3) and g is gravitational acceleration (cm/s^2).

A comparison of the predicted slag film thickness using Jeffreys model, versus that measured using the video profiling technique, is shown in Figure 10. Good agreement between the two confirms that the plate films do drain predictably (in the absence of Plateau borders) when under the influence of gravity.

Any solute (such as P_2O_5) which reduces the surface tension of the solvent (slag) is adsorbed at the surface of the solution,[15] the monomolecular surface layer thus being enriched (and possibly saturated) with tension-active solute.

The molecular structure of such surface layers may exhibit different physical properties to the bulk of the liquid slag. For instance, a slowing of the film draining rate with increasing P_2O_5 content could also be attributed to an increased surface viscosity, rather than just the lowering of surface tension.

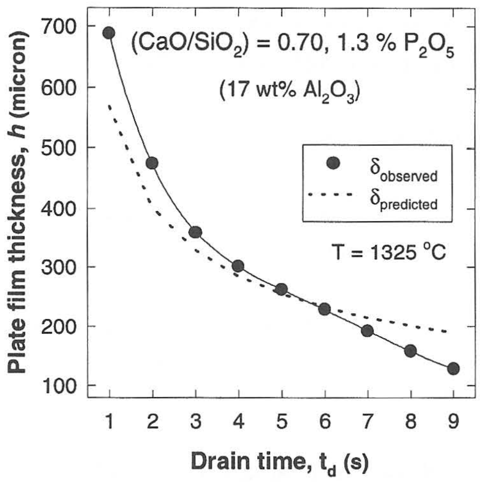

Fig.10. Measured versus predicted thickness for a plate slag film, of height 0.9 cm, at 1325 °C.

Measurement of surface viscosity in slag systems is extremely difficult, and thus its influence on the draining rate in free films would be difficult to explain using only the results presented. However, to clarify any differences between the effect of P_2O_5 on the film draining rate, comparisons were also made between the results for the free films and plate film experiments.

The aforementioned video technique was used to record and measure the rate of descent of the top of the plate films during the initial draining stages. This involved recording (with a stop-watch), the time required for the top section of the film to descend through a fixed distance of 0.9 cm. The results shown in Figure 11 are for a slag with a fixed basicity, but differing concentrations of P_2O_5. Addition of P_2O_5 increased the rate of film descent. This trend was also observed when comparing the relative draining rates from the gravimetric plate experiments of the same slags.

Currently, it is uncertain whether the bulk viscosity of the slag would have decreased slightly, but it has been reported[16] elswhere that addition of P_2O_5 can decrease the bulk viscosity of more basic CaO-SiO_2 slags. It is believed that if the plate films were influenced strongly by a P_2O_5 induced surface viscosity, then one would have expected to observe a decrease in the film descent rate with increasing P_2O_5 concentration, rather than the contrary.

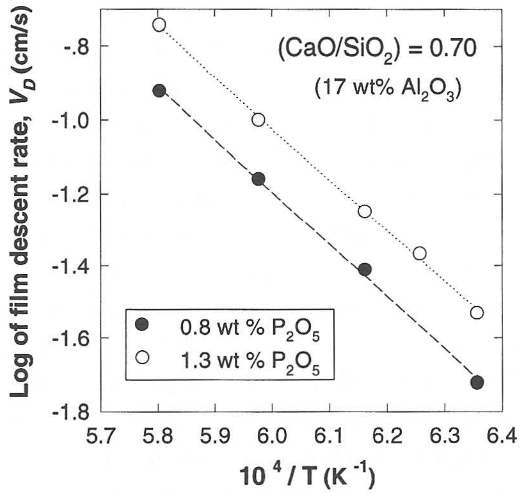

Fig.11. Effect of P_2O_5 on the rate of descent of plate slag films, of height 0.9 cm, from 1300-1450 °C.

Although not observed with the plate film experiments, a decrease in the draining rate with addition of P_2O_5 was in fact observed for the free films, as previously mentioned. This suggests that the composition of the surface layers in the free films are likely to be significantly influenced by the presence of a strongly adsorbed surfactant. An increase in the film elasticity is likely to be the most important contribution for the observed decrease in the draining rates of the free films, the concentrations of P_2O_5 added should be below that for surface saturation, thus minimizing any strong influence from surface viscosity.

The effect of P_2O_5 on slag films having a higher basicity (such as 1.20) has commenced, as has substitution of P_2O_5 with a more basic surface active oxide such as Na_2O. This may shed some light on any influence surface viscosity may have in the draining of slag films.

4. CONCLUSION.

High temperature gravimetric "free" film experiments on $CaO-SiO_2-Al_2O_3$ slags have shown that the draining rate and film life are strongly influenced by temperature. The average film thicknesses were found to be orders of magnitude greater than those encountered in typical soap films. The effect of viscosity (basicity) on the rate is still unclear, as the rate was found to decrease with increasing basicity. The addition of P_2O_5 as a surfactant decreased the film draining rate markedly (irrespective of temperature), and had minimal effect on film life. Possible causes of the rate decrease with decreasing surface tension could be due to a lowering of the Laplace pressure operating within the films (thus decreasing the Plateau border suction), or an increase in film elasticity. The observed and measured parabolic thickness profiles of the "plate" films, and their good agreement with those predicted by Jeffreys model, confirm that they are more "rigid" and are strongly influenced by the bulk viscosity (in the absence of Plateau borders). Real time observations and measurement of thickness profiles of the free films using laser interferometry showed that non-uniform thinning does in fact occur. This observation is consistent with the behavior of "mobile" films, which are generally dominated by surface tension phenomena such as the Marangoni elasticity effect. Surface tension is thus likely to be the dominating stability mechanism in $CaO-SiO_2-Al_2O_3$ slag films.

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