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# Studies on bubble films of molten slags

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Bubble films of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slags were withdrawn on wire frames, and their draining rates measured at temperatures up to 1723 K using a developed gravimetric technique. The influence of additions of  $\text{Na}_2\text{O}$  and  $\text{P}_2\text{O}_5$ , as surfactants, on the draining rate and stability of slag films is investigated. Characteristic draining behaviour (interfacial flow) and the thickness of the films were investigated using a laser interferometry and laser absorption/transmission method. Evidence of localized thinning regions within the slag films, and measurements of the actual thickness of the films before rupture will be presented.

**Keywords:** foams; Plateau border; film thickness; interferometry; laser absorption

## 1. Introduction

In a well drained foam of soap solution, the plane lamellae intersect to form ‘Plateau borders’ (Plateau 1861). To some extent, this is also expected for a slag foam. Due to the curvature of the surface near the Plateau border, the pressure within these borders ( $P''$ ) is much lower relative to the flatter central lamellae (films), where the pressure is essentially atmospheric ( $P'$ ). The resulting pressure differential ( $\Delta P = P' - P''$ ) creates a ‘suction’ force for the liquid to drain from the films into the Plateau borders under capillarity, and upon reaching the borders the liquid then proceeds to drain under the influence of gravity. For very thin films (how thin they are depends on the chemistry of the solution), a ‘disjoining pressure’  $\Pi$ , originally suggested by Derjaguin & Titievskaya (1953), could become significant to counter the suction due to the curvature of the surface. The net capillary force is therefore given by  $\Delta P = 2\gamma/r - \Pi$ , where  $\gamma$  is the liquid surface tension and  $r$  is the radius of curvature of the liquid surface at the Plateau border. While the film draining characteristics and draining are extensively studied for aqueous systems (Mysels *et al.* 1959), our understanding of the characteristics of molten slag films is far from satisfactory. This paper presents some results of the study in determining the draining rate, the thickness, and thickness distribution of molten slag films spun on platinum wire frames. The slag used was  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ , and  $\text{P}_2\text{O}_5$  or  $\text{Na}_2\text{O}$  was added to show the effect of surfactant on the draining of slag films.

## 2. Experiment

Measurement of the draining rate of slag films was achieved using a previously described gravimetric technique (Nexhip *et al.* 1997), which involved suspension of a rectangular wire frame inside a furnace hot-zone from an electronic balance (situated above). The molten slag sample was contained in a Pt-30% Rh crucible, which could

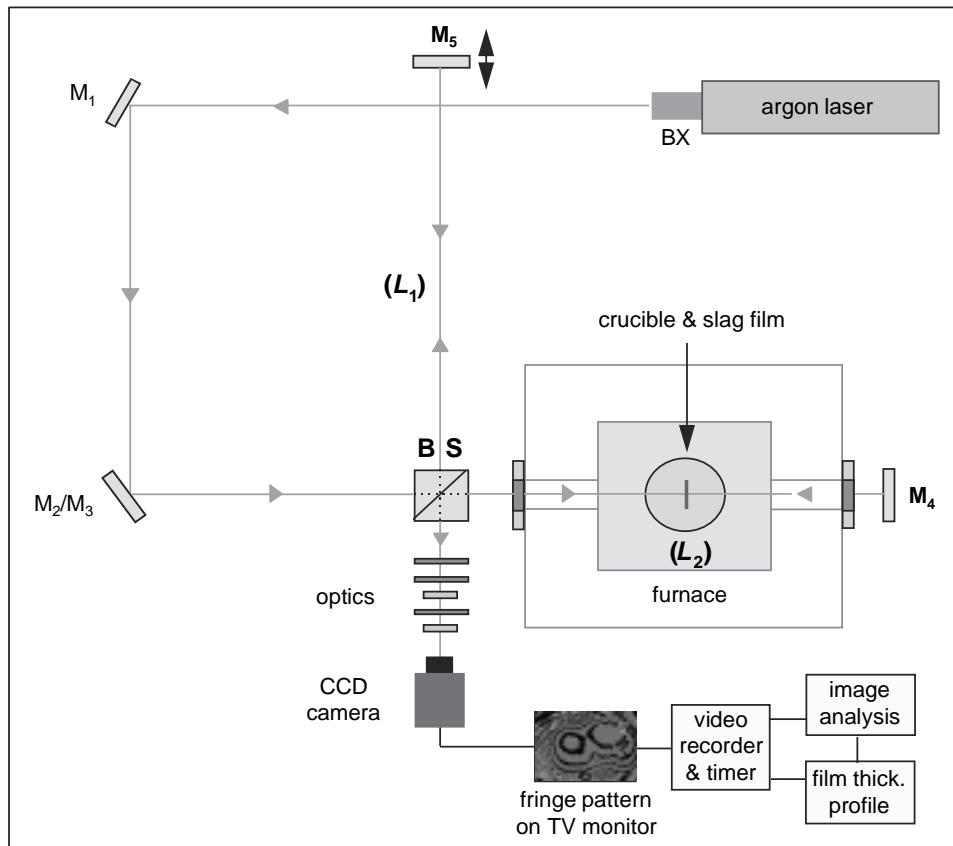


Figure 1. Michelson-type laser interferometer used for measuring the thickness profile of thinning slag bubble films.

be vertically raised or lowered using a motion actuator. Slag bubble films on the wire frames could then be formed by immersing the frame into the molten slag, and then partly withdrawing a film by lowering the crucible. As the films drained, the change in the gross mass was recorded as a function of the drain time ( $t_d$ ) until rupture occurred. The film draining rate could then be calculated from the gravimetric data. For instance, for a given slag temperature, a linear regression of the drainage data (change in mass) over a given time interval was performed, yielding the draining rate of the slag film  $V_f$  ( $\text{g s}^{-1}$ ). The drain time intervals used in the rate calculations were usually about 5 s into a draining experiment, i.e. well after the withdrawal stage where the initial recorded mass increased. For a given slag composition, up to six consecutive draining experiments were usually recorded at a given temperature and the overall rates subsequently calculated from the average of these six runs. In order to investigate the film draining behaviour in the absence of surface tension phenomena, the viscous drainage of slag films from a thin vertical plate (Jeffreys 1930) was also investigated gravimetrically; this involved withdrawing films of identical area to that of the free films.

Interferometry is a technique that has been used extensively in studies of thinning bubble films in aqueous systems (Bikerman 1973). The experimental set-up of a Michelson-type laser interferometer (Meyer-Arendt 1972), shown in figure 1, consisted of an argon-ion laser source (Spectraphysics model 2017, operating at 300 mW

and  $\lambda = 488$  nm), a BK7 beamsplitter cube (BS), and two mirrors  $M_4$  and  $M_5$  (reflectivity greater than 99%). The cube split the already expanded laser beam into two orthogonal beams, each with an approximate beam diameter of 1.0 cm. The ‘test’ beam of physical pathlength ( $L_2$ ) was transmitted through optical-quality silica windows, through the furnace hot-zone (and suspended wire frame), toward mirror  $M_4$ . The ‘reference’ beam of physical pathlength ( $L_1$ ) was reflected orthogonally toward mirror  $M_5$ , which was mounted on a horizontal translation stage. The two mirrors  $M_4$  and  $M_5$  then retro-reflected the beams, which subsequently recombined at BS where interference between the two wavefronts could be observed (when coincident) through an optics train and monochromatic CCD video camera (Pulnix model TM-6CN). After equalizing the pathlengths of  $L_1$  and  $L_2$  (by translating  $M_5$ ), the ‘zero-order’ reference fringe pattern was obtained. From here on, any change in the physical pathlength between the two interfering beams, introduced by the presence of a partly withdrawn thinning slag film, will cause a change in the relative phase of the two beams when they recombine at the beamsplitter cube; the change in phase being directly proportional to the thickness change within the film.

The thickness change ( $\Delta\delta$ ) at a given point within a given time interval could then be calculated thus (Schlesinger *et al.* 1986):

$$\Delta\delta = (m\lambda)/2(\eta_f - 1), \quad (2.1)$$

where  $m$  is an integer and represents the number of fringes counted sweeping across the point in a given time from the TV monitor during film thinning,  $\lambda$  is the wavelength of laser light (488 nm) and  $\eta_f$  is the refractive index of the liquid slag. The factor 2 in the denominator arises due to the test beam traversing the slag film twice, and the factor 1 arises from the refractive index of air taken to be unity. No data for  $\eta_f$  are available for the liquid slag used in this study. A value of 1.57 (Shelby 1985) for a glass of similar composition was used instead. The thickness change during the major part of the film life could then be calculated by dividing  $\Delta\delta$  by the total drain time ( $\Delta t$ ), over which the fringes were counted in real time, before rupture.

A laser absorption/transmission method (figure 2) was also used to measure the thickness of the films using the Beer–Lambert relationship (Takahashi & Shibata 1979):

$$I = I_0 e^{-\alpha\delta}, \quad (2.2)$$

where  $\delta$  is the film thickness,  $I$  is the intensity of a He–Ne laser beam transmitting a thinning slag film (at  $\lambda = 633$  nm),  $I_0$  is the reference intensity of the laser itself (obtained with no film present in the beam path) and  $\alpha$  is the absorption coefficient of the slag ( $\text{m}^{-1}$ ) obtained from the measurement data of Susa *et al.* (1992).

### 3. Results

The influence of small additions of surface-active oxides such as acidic  $\text{P}_2\text{O}_5$  and basic  $\text{Na}_2\text{O}$  on the draining rate (and hence stability) of ‘free’ films of  $\text{CaO–SiO}_2\text{–Al}_2\text{O}_3$  slags at 1623 K, can be seen in figure 3 where the rates ( $V_f$ ) were calculated over the drain time interval of 5–15 s. The draining rate of both  $\text{P}_2\text{O}_5$  and  $\text{Na}_2\text{O}$  containing ( $\text{CaO/SiO}_2$ )  $\sim 0.70$ , 17 wt%  $\text{Al}_2\text{O}_3$  slag films, decreased with increasing (dilute) concentration of surfactant, suggesting a decrease in the slag surface tension is likely to be responsible. The curve for the  $\text{P}_2\text{O}_5$  containing slag films appears to ‘bottom-out’ at the very dilute surfactant concentration of 0.2 wt%, the rate

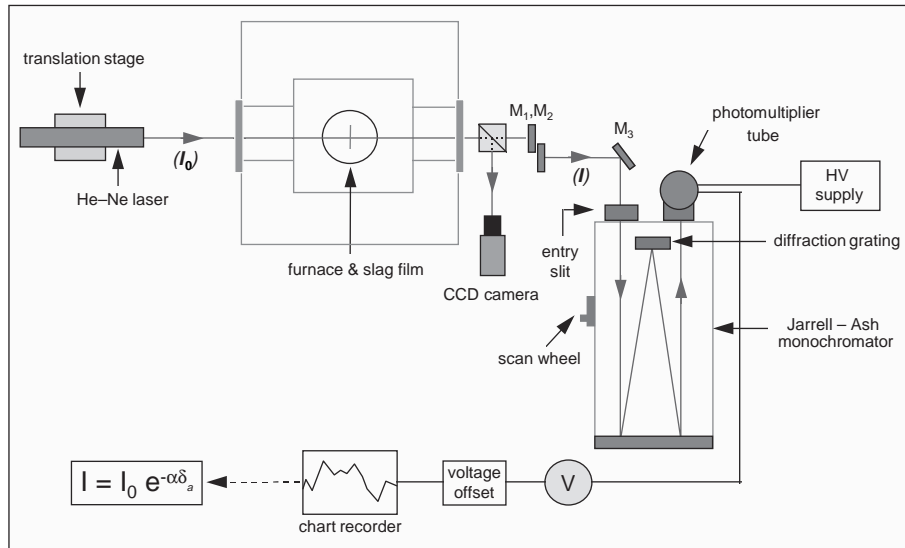


Figure 2. Absorption/transmission method for measuring the actual thickness of the thinning slag bubble films, before their rupture.

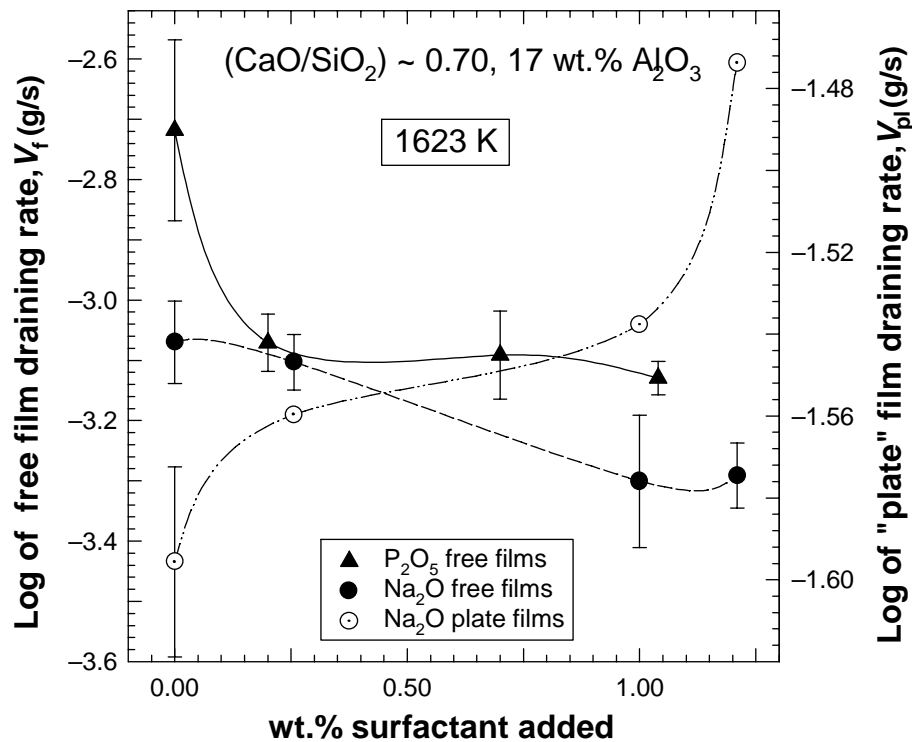


Figure 3. Calculated gravimetric draining rates of 'free' films and 'plate' films of  $(\text{CaO}/\text{SiO}_2) \sim 0.70$  slags, as a function of surfactant concentration, at 1623 K.

decreasing by a factor of about three. This implies that the films may readily become saturated at very dilute concentrations of  $\text{P}_2\text{O}_5$  in silica-rich slags. The decrease in the draining rate of  $\text{Na}_2\text{O}$ -containing films was not as dramatic, the rate decreasing

by a factor of about 1.5 at 1.0 wt% Na<sub>2</sub>O; however, the overall draining rates of the soda-containing films were lower than those for the phosphorus containing films. Presently, it is uncertain as to why the draining rates for the free films in which phosphorus and soda were absent are so different. For instance, the rate for the 0.0 wt% Na<sub>2</sub>O films are much slower than the 0.0 wt% P<sub>2</sub>O<sub>5</sub> films, despite their respective basicities being nearly identical at (CaO/SiO<sub>2</sub>) = 0.71 and 0.70. CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slag films draining from a thin (vertical) platinum plate showed the opposite trend to that observed for the free films, i.e. the plate film draining rate ( $V_{pl}$ ) increased with increasing concentration of Na<sub>2</sub>O (figure 3). The gravimetric draining curve characteristics of the plate films (not shown) were also much smoother than those of the free films, suggesting they drain more uniformly in the absence of capillary effects.

Typical laser interference fringe patterns obtained for a thinning ‘free’ film of a (CaO/SiO<sub>2</sub>) = 0.60, 15 wt% Al<sub>2</sub>O<sub>3</sub> slag at 1623 K can be seen in figure 4. What is immediately apparent is that the film thickness profile is non-uniform, and a localized thinning spot within the slag bubble lamella is seen to grow radially, eventually forming two thinning regions. From the fringe patterns obtained, the thickness of the thicker sections appear to be a few μm greater than that of the thinner sections. From equation (2.1), the calculated thickness change during the major part of the film life was about 8 μm, suggesting a thinning rate of  $\Delta\delta/\Delta t \sim 0.3\text{--}0.4 \mu\text{m s}^{-1}$ .

The results for the laser absorption/transmission experiments in figure 5 show that the measured thickness of thinning slag films decreases in the latter stage from several μm down to  $\delta \sim 0.1\text{--}0.4 \mu\text{m}$  before rupture. The figure shows the thickness at the ‘centre’ and ‘edge’ of a film to be different initially; however, during the well-drained stage the curves begin to coincide, indicating that the thickness profile across the films become very uniform. This suggests that thin (well-drained) slag films are likely to become plane-parallel before rupture, a characteristic observed within aqueous films around  $\delta < 0.1 \mu\text{m}$  (Platikanov 1964). Experiments on (CaO/SiO<sub>2</sub>) = 0.60, 15 wt% Al<sub>2</sub>O<sub>3</sub>, 9.6 wt% Fe<sub>2</sub>O<sub>3</sub> slags at 1573 K are shown in figure 6, again suggesting that the presence of dilute concentrations of P<sub>2</sub>O<sub>5</sub> in acidic (silica rich) CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slags can increase the stability of bubble films. For instance, the slag films containing 0.8 wt% P<sub>2</sub>O<sub>5</sub> ruptured at a critical thickness of about 0.38 μm (after a film life of 39 s), whereas those containing 1.3 wt% P<sub>2</sub>O<sub>5</sub> generally ruptured at a lower critical thickness of about 0.15 μm (film life of 47 s).

#### 4. Discussion

P<sub>2</sub>O<sub>5</sub> has been shown to be surface active in CaO–SiO<sub>2</sub> slags at a (CaO/SiO<sub>2</sub>) = 0.69 at temperatures of 1823–2050 K (Cooper & Kitchener 1959). The effect of Al<sub>2</sub>O<sub>3</sub> is not clearly known but is not expected to dramatically change the surface activity of P<sub>2</sub>O<sub>5</sub>. Na<sub>2</sub>O has also been shown to be surface active in CaO–SiO<sub>2</sub> slags (Swisher & McCabe 1964) and CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slags (Takayanagi *et al.* 1976), at (CaO/SiO<sub>2</sub>)  $\sim$  0.8. The influence of P<sub>2</sub>O<sub>5</sub> on the draining rate of free films of (CaO/SiO<sub>2</sub>) = 0.70, 17 wt% Al<sub>2</sub>O<sub>3</sub> slags was analogous to that usually observed in aqueous systems, i.e. the rate decreased with decreasing surface tension, which is likely to be due to a decrease in the Plateau border suction force operating within the films. The observed increase in stability through addition of P<sub>2</sub>O<sub>5</sub> to acidic CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slags could be due to the ‘cosorption’ of P<sub>2</sub>O<sub>5</sub> in a silica rich surface environment (Cooper & McCabe 1961).

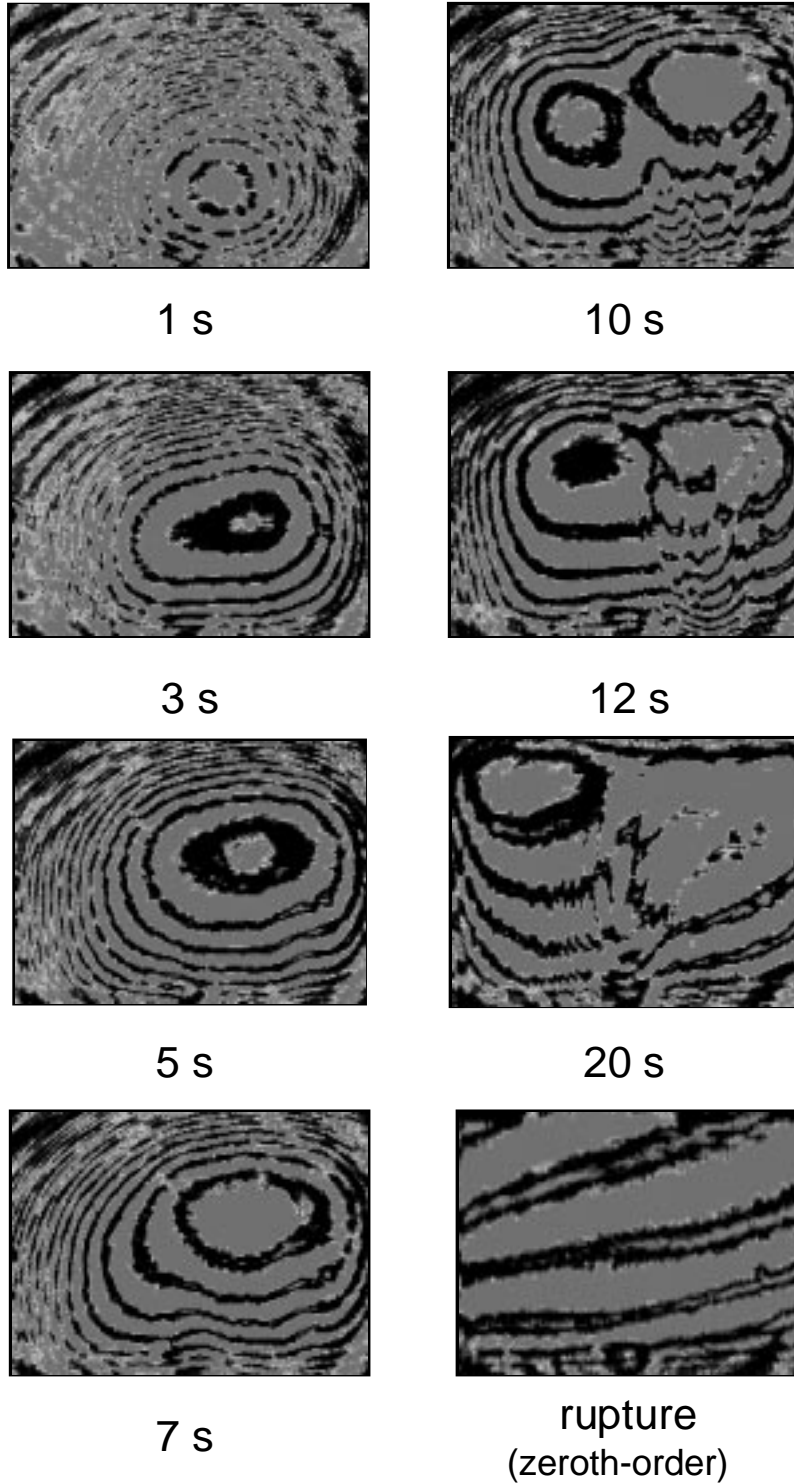


Figure 4. Laser interference fringe patterns for a thinning  $(\text{CaO}/\text{SiO}_2) = 0.60$ , 15 wt%  $\text{Al}_2\text{O}_3$  free film at 1623 K, showing a non-uniform thickness profile and localized thinning behaviour.

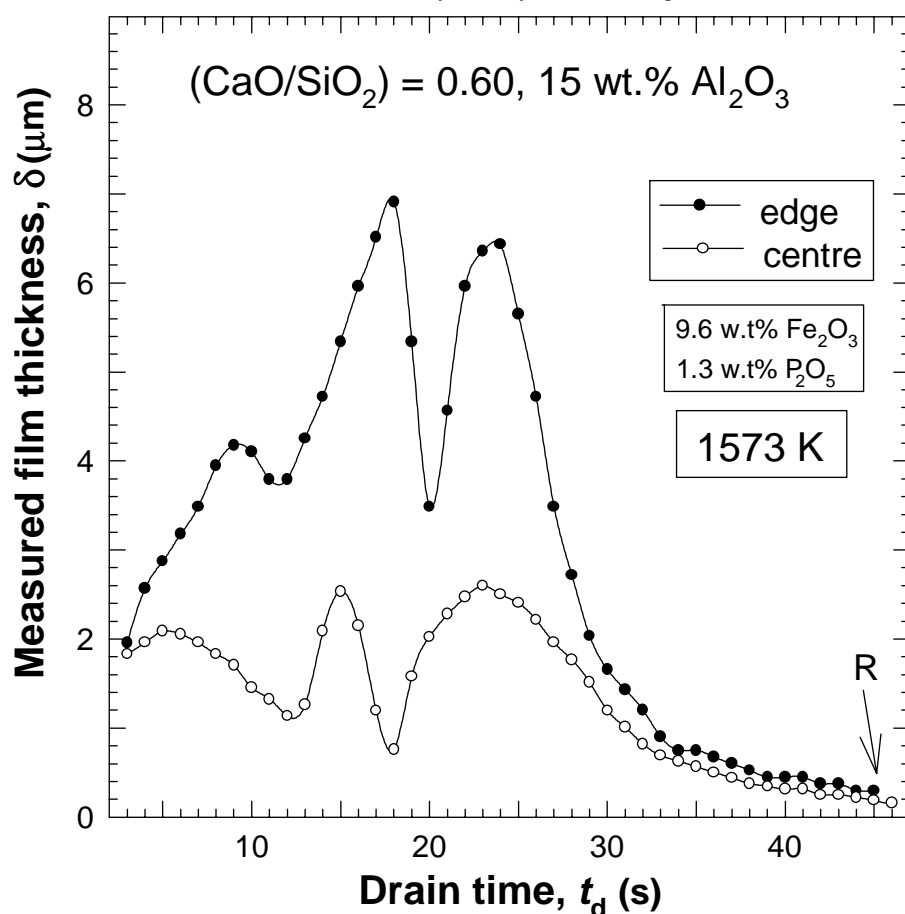


Figure 5. Laser absorption/transmission measurements of the thickness of free films of  $(\text{CaO}/\text{SiO}_2) = 0.60$ , 15 wt%  $\text{Al}_2\text{O}_3$ , 9.6 wt%  $\text{Fe}_2\text{O}_3$  slags, showing the film profile becomes uniform at the well-drained stages, before rupture at a thickness less than  $1 \mu\text{m}$ .

A high surface viscosity has been suggested to be important in increasing the stability of slag foams (Hara *et al.* 1990), as it retards liquid drainage from the lamellae. The results obtained for the addition of acidic  $\text{P}_2\text{O}_5$  to  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slags agree with this statement, i.e. an increase in  $\text{P}_2\text{O}_5$  decreased the film draining rate, which may have been due to increasing the surface viscosity of the bubble films (by polymerizing the surface). However, as already mentioned, the influence of small additions of  $\text{Na}_2\text{O}$  (as a basic surface-active oxide) to  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slags, was actually found to decrease the film draining rate. Thus the experimental results do not support the suggestion that surface viscosity significantly influences the draining rate of foam films, as the addition of  $\text{Na}_2\text{O}$  would be expected to depolymerize the surface layer and hence increase the film draining rate.

According to the present study, surface-tension lowering is likely to be the most important mechanism stabilizing the bubble films in a slag foam, as the draining rate decreased markedly when the surface tension was decreased with the addition of both acidic and basic surface-active oxides. Rather than the absolute value of the surface tension being important, the rate of change of surface-tension depression per unit concentration change of surfactant ( $d\gamma/dC$ ) has been acknowledged to be a more





patterns also suggest the thickness across the films becomes uniform/plane-parallel before their rupture.

## 5. Conclusions

Studies on 'free' films of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slags at  $(\text{CaO/SiO}_2) \sim 0.7$ , have revealed that the presence of strong surfactants such as acidic  $\text{P}_2\text{O}_5$  and basic  $\text{Na}_2\text{O}$  markedly decrease the draining rate of the bubble films. Surface-tension lowering ability (or effective elasticity,  $d\gamma/dC$ ) is likely to be the most important mechanism influencing the drainage of slag bubble films, i.e. a lower surface tension will result in a decrease in the Plateau border suction force. This conclusion was supported by the fact that the addition of  $\text{Na}_2\text{O}$  to the aforementioned slag actually increased the draining rate of 'plate' films, in which capillary forces are insignificant. The surfaces of free films of a  $(\text{CaO/SiO}_2) = 0.60$ , 15 wt%  $\text{Al}_2\text{O}_3$  slag were also shown to be non-uniform in thicknesses, with localized thinning occurring within the lamella. At the well-drained stage, slag bubble films are likely to become plane-parallel, with rupture occurring at thicknesses around 0.1–0.4  $\mu\text{m}$ .

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## References

- Bikerman, J. J. 1973 *Foams*, pp. 65–97, 149–158. New York: Springer.
- Cooper, C. F. & Kitchener, J. A. 1959 *JISI* **193**, 48–55.
- Cooper, C. F. & McCabe, C. L. 1961 Physical chemistry of process metallurgy. *Met. Soc. Conf.* **7**, pt 1, 117–131.
- Derjaguin, B. V. & Titievskaya, A. S. 1953 *Kolloid Zh.* **15**, 416.
- Hara, S., Kitamura, M. & Ogino, K. 1990 *ISIJ Int.* **30**, 714–721.
- Jeffreys, H. 1930 *Proc. Camb. Phil. Soc.* **26**, 204.
- King, T. B. 1964 *Trans. Met. Soc. AIME* **230**, 1671.
- Meyer-Arendt, J. R. 1972 *Introduction to classical and modern optics*. Englewood Cliffs, NJ: Prentice-Hall.
- Mysels, K. J., Shinoda, K. & Frankel, S. 1959 *Soap films, studies of their thinning*. London: Permagon.
- Nexhip, C. 1997 Fundamentals of foaming in molten slag systems. Ph.D. thesis, University of Melbourne.
- Nexhip, C., Sun, S. & Jahanshahi, S. 1997 Drainage of molten  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slag films. *Proc. 5th Int. Conf. on Molten Slags, Fluxes and Salts, Sydney*, p. 297. Warrendale, PA: Iron and Steel Society.
- Plateau, J. 1861 *Mem. Acad. R. Sci. Belg.* **33**, 5th and 6th series.
- Platikanov, D. 1964 *J. Phys. Chem.* **68**, 3619.
- Schlesinger, M., De Kee, D. & Godo, M. N. 1986 *Rev. Sci. Instrum.* **57**, 2535–2537.
- Shelby, J. E. 1985 *J. Am. Ceram. Soc.* **68**, 155–158.
- Susa, M., Futao, L. & Nagata, K. 1992 *Proc. 4th Int. Conf. on Molten Slags and Fluxes, Sendai*, pp. 22–27. ISIJ, 1-9-4, Otemachi Chiyoda-ku, Tokyo, Japan.
- Swisher, J. H. & McCabe, C. L. 1964 *Trans. Met. Soc. AIME* **230**, 1669–1675.
- Takahashi, S. & Shibata, S. 1979 *J. Non-Crystall. Solids* **30**, 339.
- Takayanagi, T., Kato, M. & Minowa, S. 1976 *J. Jap. Foundry Soc.* **48**, 779.
- Phil. Trans. R. Soc. Lond. A* (1998)

*Discussion*

S. K. WILSON (*Department of Mathematics, University of Strathclyde, Glasgow, UK*). Could Professor Nexhip give us an indication of the typical size of surfactant gradients in the experiments, i.e. whether or not the role of the surfactant is primarily to change the mean value of surface tension or to create surface-tension gradients? If surface-tension gradients are significant then the author might be interested in contacting Dr J. R. Ockendon's group at the Oxford Centre for Industrial Applied Mathematics (Oxford University), who are currently undertaking a theoretical investigation of the effects of surface-tension gradients in foam drainage.

C. NEXHIP. Dr Wilson has certainly identified a very interesting issue in the capillary-driven flow in a liquid film. Both the lowering of the surface tension by the addition of a surfactant and the non-uniform distribution of the surfactant on the surface could have implications on the draining of liquid films. However, to our best knowledge, there have been no direct measurements of the 'surface' composition of a molten slag. Almost all information regarding the surface composition of a molten slag is derived from surface-tension data together with the Gibbs adsorption isotherm. In other words, all these refer to the equilibrium state. Under transient or dynamic conditions, spatial variation of the surface tension may be taken to imply that a surfactant gradient exists on the surface. Unfortunately, no conclusive experimental knowledge is available regarding this gradient.

In summary, the surface excess of surfactants in a molten slag is usually inferred from equilibrium measurements. No firm indication can be given for the surfactant gradient. For that reason, other approaches to the investigation in surfactant gradients (such as the suggested work by Dr J. R. Ockendon's group) could be interesting.

M. MCLEAN (*Department of Materials, Imperial College, London, UK*). The big difference in the draining rates of two nominally identical slags with *no* added surfactant requires some comment (see figure 3). Does this indicate that the results are particularly sensitive to the slag composition (apart from surfactant) or that the measurements are due to a high level of uncertainty?

C. NEXHIP. The  $P_2O_5$  and  $Na_2O$ -free slags had the same target composition. However, as shown in figure 3, the draining rate for the 'surfactant free' slag from the  $Na_2O$  series was noticeably lower than that from the  $P_2O_5$  series of experiments. It is currently uncertain as to why the two draining rates were so different. Two factors could have contributed to it. Firstly, the samples used were from two batches. All samples were prepared from a premelted master slag of 18%  $Al_2O_3$  with  $CaO/SiO_2 = 0.93$ , by adding a specified amount of  $SiO_2$  to get the desired  $CaO/SiO_2$  ratio. Unlike the sample for the  $P_2O_5$  series, which was prepared from a fresh batch of the master slag, the one for the  $Na_2O$  experiments was from a batch that had been used earlier in a series of 'surfactant-free' draining experiments. Secondly, the  $Na_2O$  series of experiments were carried out after the  $P_2O_5$  experiments, and there was some evidence of  $P_2O_5$  loss in the earlier experiments. Thus any  $P_2O_5$  deposited on the furnace interior could have become a surface contaminant in the  $Na_2O$ -free containing slags (used subsequently).