The Prediction of Gas Residence Times in Foaming $\text{CaO-SiO}_2\text{-FeO}$ Slags

Surinder S. GHAG, Peter C. HAYES¹⁾ and Hae-Geon LEE²⁾

RGC Mineral Sands, Capel, WA 6271, Australia.

1) Department of Mining, Minerals and Materials Engineering, The

University of Queensland, Brisbane, Qld 4072, Australia.

2) Department of Materials Science and Metallurgical Engineering, Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-ku, Pohang, 790-784, Korea.

(Received on October 31, 1997; accepted in final form on June 22, 1998)

A dynamic, non-equilibrium model of foaming:

$$\Sigma = 1 \times 10^6 \left(\frac{\mu \cdot E_{\text{eff}}}{(\rho g)^2 d^3} \right)$$

which relates the residence times of gas bubbles in foams (Σ) to the viscosity of the liquid phase (μ); the effective elasticity (E_{eff}) resulting from the dynamic adsorption of surface active species; the liquid phase density (ρ); and the mean bubble diameter (d); has been applied to foaming in the $\text{CaO-SiO}_2\text{-FeO}$ system at 1823 K.

In agreement with industrial observations, the model shows a transition from a foaming regime to a non-foaming regime as the slag basicity increase above 1.5. This is due to poor surface elasticity resulting from the negligible adsorption of silica in this region.

KEY WORDS: slag; foaming; physical modelling.

1. Introduction

The high rates of gas injection in smelting reduction process may, in the presence of a sufficient quantity of slag, result in a substantial increase in the volume and interfacial area of the gas-in-slag dispersion, in a phenomenon known as slag foaming. The increase in the apparent slag volume resulting from the retention of gas bubbles within the slag phase can have a considerable impact on the efficiency of smelting operations.¹⁾ It is therefore necessary to understand the mechanisms of gas bubble retention within the slag phase in order to control the slag foaming phenomena.

Recently a model of foaming has been developed^{2,3)} that directly considers the effect of the dynamic adsorption of surface active species on foaming, rather than indirectly through the equilibrium surface tension or surface tension depression. The model shows that the structure of the foam and the gas retention within the foam are dependent on the dynamics of the bubble rupturing processes.³⁾ In its simplest form (for close-packed spherical foams with minimal internal coalescence of bubbles) this model shows that, in the regime of linearity between the foam height and gas flux, the residence times of gas bubbles (Σ) in foams stabilised by viscoelastic force is directly proportional to the viscosity of the liquid phase (μ) and the effective elasticity (E_{eff}), and inversely proportional to the square of the liquid phase density (ρ) and the cube of the mean bubble

diameter (d):

$$\Sigma = 1 \times 10^6 \left(\frac{\mu \cdot E_{\text{eff}}}{(\rho g)^2 d^3} \right) \quad (\text{s}) \quad \dots\dots\dots(1)$$

with all properties in SI units.

Measurements on the rupture thicknesses of slag films⁴⁾ show these films to rupture at thicknesses too large for the foam to be stabilised by interaction forces in thin films. Therefore it is reasonable to conclude that, of the two mechanisms for film stabilisation, *i.e.*, elastic forces and interaction forces, slag foams, like the wet spherical foams used to derive the above model, are stabilised by viscoelastic forces. Consequently Eq. (1) can be used for the calculation of gas residence times in slag forms.

The $\text{CaO-SiO}_2\text{-FeO}$ system has been selected for this analysis because it is the fundamental system for both ferrous and non-ferrous smelting. It has been shown previously^{2,3)} that relatively large bubbles (5–20 mm) produced gas injection into slags are unlikely to produce a foam. Consequently the foam is considered to be generated by gas evolved as a result of chemical reactions between the slag and molten metal. In applying the model, the slag and melt are assumed to be held in a non-reacting crucible, and the system is at steady-state such that neither the composition nor the volume of the phase change with time.

Fig. 1. The densities of CaO-SiO₂-FeO slags at 1823 K – calculated from models of Mills and Keene.⁷⁾

Fig. 2. The viscosities of CaO-SiO₂-FeO slags at 1823 K – calculated from the Urbain's Model.^{7,8)}

2. Calculation of System Properties

Equation (1) shows that data on the viscosity, density, and effective elasticity of the slag, together with the gas bubble size, is required to calculate gas residence times. The cold modelling investigation³⁾ has shown that the effective elasticity can be calculated from a combination of the isotherm for silica adsorption and diffusion models. This procedure requires data on the surface tension of the system, and the activity and diffusion coefficients of the surface active species in the slag.

Noting that silica is the most surface active species in the CaO-SiO₂-FeO system,⁵⁾ and the activity of silica in the ternary system has been calculated by Gibbs-Duhem integration from the measured activity of FeO in CaO-SiO₂-FeO system at 1823 K⁶⁾; a base temperature of 1823 K has been selected for the calculations.

The densities of CaO-SiO₂-FeO melts at 1823 K have been calculated from empirical models⁷⁾ which shows that the slag density increases with iron oxide content—Fig. 1. The viscosities of CaO-SiO₂-FeO melts have been calculated from Urbain's model.^{7,8)} Within the uncertainty of 20–30% in the model,⁷⁾ the viscosity is constant for a constant silica content, and increases markedly with increasing silica content of the slag—Fig. 2. The procedure for the calculation of the elasticities of slag surfaces follows that used for the low temperature system.³⁾ The calculation of the elasticities of the slags requires data on the activity of silica, surface tensions of the slags, diffusivity of silica, and the oscillation frequencies of the gas bubbles. Whilst the activity of silica in this system is obtained from the literature⁶⁾ the other properties will be discussed below prior to the calculation of the effective elasticity.

Measurements of the surface tensions of CaO-SiO₂, FeO-SiO₂, and FeO-CaO melts are remarkable for the lack of consistency between investigations.^{5,9–14)} For the calcium silicate system, the results of Cooper and Kitchener¹⁰⁾ are the median values and in excellent agreement with those of Gunji and Dan.¹¹⁾ Furthermore,

the shape of the surface tension-silica concentration curves for calcium silicates does not vary significantly between studies.^{5,10)} However, this is not the case for calcium ferrites, where the minimum in the surface tensions at 1673 K reported by Kozakevitch¹²⁾ is not observed in studies by Kawai *et al.*¹³⁾ at 1673 K and Kidd and Gaskell⁹⁾ at 1683 K. Although both sets of latter authors found lime to be only mildly surface active in the melts, the results of Kawai *et al.* are lower than those of Kidd and Gaskell by more than 50 mN/m. In the FeO-SiO₂ system the results of Kawai *et al.*¹³⁾ and Kidd and Gaskell⁹⁾ are in good agreement except for silica contents of less than 10 mol%. Similarly, Kidd and Gaskell found reasonable agreement with the results of Kozakevitch¹²⁾ and King¹⁴⁾ for iron silicate melts containing more than 20 wt% FeO. Examination of the data of Kawai *et al.*¹³⁾ and Kidd and Gaskell⁹⁾ for the surface tensions of iron silicate and calcium ferrite melts shows that the discrepancies between these investigations are due to differences in the measured surface tension of FeO. Whereas the former authors measured the surface tension of FeO to be 515 mN/m at 1673 K, the latter obtained a value of 577 mN/m at 1683 K. Clearly, the surface tension data is not sufficiently accurate for the determination of the adsorption isotherm. Therefore a subset of the above data has been selected to calculate the isotherm. This subset consists of the measurements of Cooper and Kitchener¹⁰⁾ and Gunji and Dan¹¹⁾ on calcium silicate slags, and the surface tension of pure iron oxide in equilibrium with iron. Due to the differences in the measured surface tension of FeO discussed above, the values of both the studies of Kidd and Gaskell⁹⁾ and Kawai *et al.*¹³⁾ are used in the present investigation, resulting in two isotherms for the system.

In determining the adsorption isotherm, the simplifying assumption has been made that silica is the only surface active species in the melt. Measurements on the surface tensions of FeO-CaO^{9,13)} show that CaO is only weakly surface active in comparison to SiO₂. Considering that the relative surface excess of FeO is equal to zero, the Gibbs adsorption isotherm is simplified to:

$$\Gamma_{\text{SiO}_2} = -\frac{1}{RT} \frac{d\sigma}{d \ln a_{\text{SiO}_2}} \quad \text{.....(2)}$$

where Γ_{SiO_2} is the Gibbs relative surface excess of silica, σ is the surface tension of the slag, and a_{SiO_2} is the silica activity. If it is assumed that the adsorption of silica follows Langmuir behaviour, the following relationship is obtained between the relative surface excess of silica and the silica activity^{15,16}:

$$\Gamma_{\text{SiO}_2} = \Gamma_{\text{SiO}_2, \infty} \frac{K_a \cdot a_{\text{SiO}_2}}{1 + K_a \cdot a_{\text{SiO}_2}} \quad \text{.....(3)}$$

where $\Gamma_{\text{SiO}_2, \infty}$ is the Gibbs relative surface excess of silica at saturation of the surface, and K_a is the adsorption coefficient. Equation (3) can be expressed in the following form:

$$\Gamma_{\text{SiO}_2} = \Gamma_{\text{SiO}_2, \infty} \frac{a_{\text{SiO}_2}}{a_{\text{SiO}_2} + a_{\text{SiO}_2, L}} \quad \text{.....(4)}$$

in which case:

$$K_a = \frac{1}{a_{\text{SiO}_2, L}} \quad \text{.....(5)}$$

where $a_{\text{SiO}_2, L}$ is equivalent to the silica activity at which the Gibbs relative surface excess of silica is equal to half the saturation value.

Substituting Eq. (4) into Eq. (2) and integrating with the boundary condition that $\sigma = \sigma_0$ when $a_{\text{SiO}_2} = 0$:

$$\sigma = \sigma_0 - RT \Gamma_{\text{SiO}_2, \infty} \ln \left(1 + \frac{a_{\text{SiO}_2}}{a_{\text{SiO}_2, L}} \right) \quad \text{.....(6)}$$

results in the theoretical equivalent to Szyszkowski's empirical equation.^{15,16} The surface tension of the system without silica, σ_0 , is equal to the surface tension of iron oxide, σ_{FeO} . The assumption that CaO is not surface active in the system is then equivalent to considering the surface tension of CaO to be equal to that of FeO.¹⁷ Obviously the surface tension of lime at 1823 K is effectively a virtual surface tension because CaO is not present as a liquid phase at this temperature.

The surface tensions at 1823 K have been calculated from the data discussed above using a mean temperature coefficient of -0.1 mN/m/K .⁹ Equation (6) has been fitted to the calculated data using the procedure described previously.² The following adsorption isotherms are obtained, depending on whether the surface tension of FeO at 1823 K is calculated from the data of Kidd and Gaskell⁹:

$$\sigma = 563 - 2.66 \times 10^{-3} RT \ln \left(1 + \frac{a_{\text{SiO}_2}}{0.0159} \right) \quad \text{.....(7)}$$

or Kawai *et al.*¹³:

$$\sigma = 500 - 4.08 \times 10^{-3} RT \ln \left(1 + \frac{a_{\text{SiO}_2}}{0.206} \right) \quad \text{.....(8)}$$

The calculated relative surface excess of silica at saturation of 2.66×10^{-6} and $4.08 \times 10^{-6} \text{ mol/m}^2$ are in good agreement with the values determined by Kidd and Gaskell.⁹ Although the ideal behaviour of the slag

Fig. 3. The surface tensions of CaO-SiO₂-FeO slags as a function of silica activity at 1823 K. Also shown are the surface tensions predicted from Eqs. (7) and (8).

Fig. 4. The calculated surface tensions for CaO-SiO₂-FeO slags at 1823 K. Surface tensions calculated from the data of Kidd and Gaskell⁹ for the surface tension of FeO-Eq. (7).

surface may at first be somewhat surprising considering that the bulk slag is non-ideal, similar behaviour is observed in numerous air-water, oil-water and solid-liquid interfaces.¹⁸ The surface tension data used to determine these isotherms is shown in Fig. 3 together with Eqs. (7) and (8). The figure shows that silica is more surface active in the isotherm based on the FeO surface tension data of Kidd and Gaskell⁹ than the data of Kawai *et al.*¹³ the adsorption coefficients for silica are 62.9 and 4.85, respectively.

The surface tensions of the CaO-SiO₂-Fe-O system calculated from Eqs. (7) and (8) have been plotted in Figs. 4 and 5, which show that the adsorption of silica on the surface of the CaO-SiO₂-Fe-O melts is negligible for basicities greater than approximately 1.5. It is clear from Fig. 4 that if the surface tension of FeO at 1823 K is closer to 560 mN/m rather than 500 mN/m, then as

Fig. 5. The calculated surface tensions for CaO-SiO₂-FeO slags at 1823 K. Surface tensions calculated from the data of Kawai *et al.*¹³⁾ for the surface tension of FeO-Eq. (8).

the slag basicity decreases below 1.5 there is a rapid increase in silica adsorption, and the surface tension decreases markedly in this region due to a fifty-fold decrease in silica activity in this region.⁶⁾

The Marangoni dilational modulus (E_M) has been calculated from Eqs. (7) and (8) using the procedure described previously,³⁾ resulting in the following equations depending on whether the adsorption isotherm is based on the surface tension data of Kidd and Gaskell⁹⁾:

$$E_M = 2536a_{\text{SiO}_2} \quad (\text{mN/m}) \quad \dots\dots\dots(9)$$

or Kawai *et al.*¹³⁾:

$$E_M = 300a_{\text{SiO}_2} \quad (\text{mN/m}) \quad \dots\dots\dots(10)$$

The Marangoni dilational modulus has been plotted in Fig. 6 using Eqs. (9) and (10) and the silica activity.⁶⁾ It is evident from the figure that the isotherm based on the data of Kidd and Gaskell⁹⁾ (Eq. (9)) results in significantly higher Marangoni dilational moduli.

Although the calculated Marangoni dilational moduli of the CaO-SiO₂-FeO slags are significantly higher than those of the aqueous system,³⁾ it would be premature to conclude that the slag will foam more readily than the water-glycerol-SDBS system because the effects of adsorption time and frequency of bubble oscillation have not been examined.

The effect of adsorption time on the relative surface excess of silica can be determined from the model described previously^{3,19)} because the adsorption of silica has been shown to follow ideal (Langmuir) behaviour. In applying the model to slag foaming, the equilibrium relative surface excess of silica for a particular slag composition is calculated from Eq. (4), and the corresponding molar silica concentration (c_{SiO_2}) is calculated from the molar volume of the slag⁷⁾ (V^m) and the mole fraction of silica (x_{SiO_2}):

$$c_{\text{SiO}_2} = \frac{1000x_{\text{SiO}_2}}{V^m} \quad \dots\dots\dots(11)$$

to maintain dimensional consistency. Furthermore, the

Fig. 6. The Marangoni dilational modulus of CaO-SiO₂-FeO slags at 1823 K. The values not enclosed in brackets have been calculated from Eq. (9) while those in brackets have been calculated from Eq. (10).

reduced activity ($a_{\text{SiO}_2}/a_{\text{SiO}_2,L}$) is used rather than the reduced concentration ($c_i/c_{i,L}$).

The interdiffusivity of silica (D) in the CaO-SiO₂-Fe-O systems has not been measured. However, the self diffusion of tracer silicon has been measured at 1873 K in the binary CaO-SiO₂ system.²⁰⁾ Johnston *et al.*²¹⁾ note that the self diffusivity may be used in mass transfer calculations without introducing significant error.

The Stokes-Einstein equation:

$$D_{AB} = \frac{kT}{6\pi\mu r_A} \quad \dots\dots\dots(12)$$

where k is the Boltzman constant, and r_A is the radius of the diffusing species, has been applied to the experimental data of Keller and Schwerdtfeger to estimate the diffusion coefficient at temperatures other than 1873 K. However, Eq. (12) is strictly only applicable to dilute solutions of small solutes. Geankoplis²²⁾ found that the exponent of the viscosity term in the Stokes-Einstein equation lies within the range 0.5–1 for viscous solutions. Plotting the diffusivity of silicon tracer at 1873 K as a function of the slag viscosity in Fig. 7 it can be seen that an excellent regression fit is obtained for the data:

$$D = \frac{3.04 \times 10^{-11}}{\mu^{0.886}} \quad \dots\dots\dots(13)$$

with regression coefficient of 0.995. Therefore the diffusivity of silica in calcium silicate slags at a specific temperature is considered to be equal to:

$$D = \frac{T}{1873} \frac{3.04 \times 10^{-11}}{\mu^{0.886}} \quad \dots\dots\dots(14)$$

Furthermore, the effect of iron oxide on the diffusivity of silica in CaO-SiO₂-Fe-O slags has been accounted for by its influence on the viscosity in Eq. (14). The results of these calculations are shown in Fig. 8 which shows that the diffusivity of silica is constant for a fixed silica concentration, and decreases with increasing silica

Fig. 7. The self-diffusivity of tracer silicon²⁰⁾ in CaO–SiO₂ slags at 1873 K as a function of slag viscosity.⁶⁾ Also shown is the diffusivity predicted from Eq. (13).

Fig. 8. The diffusivity of silica in CaO–SiO₂–FeO slags at 1823 K as calculated from Eq. (14).

content of the slag because the slag viscosity increases.

The effect of adsorption time on the fraction of equilibrium coverage can be determined as described previously.^{3,19)} The results of these calculations for the binary calcium silicate slags are shown in Fig. 9. In view of the extremely fast rate of adsorption of silica evident in the figure, it is reasonable to conclude that the maximum elasticity in CaO–SiO₂–Fe–O slags is not limited by the adsorption time.

The model for determining the effect of oscillation frequency on the elasticity has been discussed previously.³⁾ For this model it can be shown that the parameter, A_1 , has to be modified to:

$$A_1 = \frac{\Gamma_{\text{SiO}_2, \infty} \cdot a_{\text{SiO}_2} \cdot a_{\text{SiO}_2, L}}{D \cdot c_{\text{SiO}_2} (a_{\text{SiO}_2} + a_{\text{SiO}_2, L})^2} \quad \text{.....(15)}$$

in order to express the model in terms of the activity of silica rather than the molar concentration, and at the same time maintain dimensional homogeneity.²³⁾ The

Fig. 9. The effect of adsorption time on the fraction of equilibrium adsorption in CaO–SiO₂ melts at 1823 K.

Fig. 10. The effective elasticity (based on the data of Kidd and Gaskell⁹⁾ for the surface tension of FeO) of CaO–SiO₂–FeO slags at 1823 K oscillating at a frequency of 1000 Hz.

oscillation frequency is retained as an independent parameter with frequencies in the range 10–1 000 Hz used to calculate the effective elasticity.

The effective elasticity calculated from the adsorption isotherm based on the data of Kidd and Gaskell⁹⁾ (Eq. (7)) has been plotted in Figs. 10 and 11 for oscillation frequencies of 1 000 and 100 Hz, and for the data based on the surface tension data of Kawai *et al.*¹³⁾ for an oscillation frequency of 1 000 Hz in Fig. 12. A number of conclusions can be drawn from the results.

Firstly, it is readily observed that, unlike the aqueous water–glycerol–SDBS system at 293 K, where the effective elasticities are within ten percent of the Marangoni dilational modulus for some compositions, the effective elasticities of silica adsorbed films in CaO–SiO₂–FeO slags are generally four to five orders of magnitude lower than the Marangoni dilational modulus (Fig. 6) of these slags, and more than three orders of magnitude lower

Fig. 11. The effective elasticity (based on the data of Kidd and Gaskell⁹⁾ for the surface tension of FeO) of CaO-SiO₂-FeO slags at 1823 K oscillating at a frequency of 100 Hz.

Fig. 12. The effective elasticity (based on the data of Kawai¹³⁾ for the surface tension of FeO) of CaO-SiO₂-FeO slags at 1823 K oscillating at a frequency of 1000 Hz.

than the elasticities of the water-glycerol-SDBS system.³⁾ The very low elasticities of the slags are due to high rates of diffusional mass transfer to the oscillating bubble film surfaces resulting from high silica concentrations in the bulk phase.

Furthermore, comparison of the figures based on the two distinct isotherms shows that the effective elasticities are dependent on the isotherm used. A maximum in the effective elasticities at low silica concentrations is evident in Figs. 10 and 11 but not in Fig. 12. The high elasticities present in this region are due to a combination of the high surface activity of silica in the isotherm based on the data of Kidd and Gaskell⁹⁾ (the adsorption coefficient is 62.9 for the isotherm based on the data of Kidd and Gaskell⁹⁾ and 4.85 for the isotherm based on the data of Kawai *et al.*¹³⁾), and low bulk concentrations limiting diffusional mass transfer which would otherwise diminish the elasticity. For the isotherm based

on the data of Kawai *et al.*,¹³⁾ silica is not sufficiently surface active to produce a significant elasticity at low silica concentrations.

Although the absolute magnitudes of the elasticities are also dependent on saturation coverage of silica in the two isotherms, a common feature of the elasticities calculated from the two isotherms is that for slags with a basicity of more than approximately 1.5, the elasticity decreases by two orders of magnitude over a narrow composition range. This is due to fifty-fold decrease in the activity of silica in this region.⁶⁾

Comparison of the effective elasticities shown in Figs. 10–12 with the calculated equilibrium surface tensions in Figs. 4 and 5, clearly shows that a simple relationship does not exist between the effective elasticities and surface tensions of these slags. Therefore modelling slag foaming in terms of the equilibrium surface tensions of slags will lead to erroneous conclusions.

In terms of the oscillation frequency, examination of Figs. 10–11 shows that the effective elasticity is proportional to the square root of the oscillation frequency.

3. Calculation of Gas Residence Times

The residence times of gas bubbles in CaO-SiO₂-FeO slags have been determined from Eq. (1) using the calculated values for the physico-chemical properties. Typical examples are shown in Figs. 13 and 14 for constant bubble sizes of 2 and 1 mm diameter, with the effective elasticities calculated from the data of Kidd and Gaskell⁹⁾ for an arbitrarily chosen oscillation frequency of 1 kHz. It is evident from the figures that, for fixed bubble sizes, the residence times increase with increasing silica content of the slags. This results from increasing viscosities (Fig. 2) and effective elasticities (Figs. 10–12) of the slags, and decreasing densities (Fig. 1) with increasing silica content. The gas residence times for other bubble sizes can readily be determined from Eq. (1).

Figures 13 and 14 also show that for slags with basicities above approximately 1.5, the gas residence times of the 1–2 mm diameter bubbles are negligible. In general, it was found that for all but the 0.1 mm diameter bubbles, the gas residence times in this region are less than one second.²³⁾ The cold model study^{2,23)} has shown that residence times of this magnitude are indicative of non-foaming rather than foaming dispersions. Consequently the application of the present model to slag foaming predicts a transition from non-foaming to foaming CaO-SiO₂-FeO slags in this region. This is consistent with the results of Cocchiarella *et al.*²⁴⁾ who observed significant foaming (foam heights of 5 m) in a 300 t K-OBM furnace as the basicity was reduced to 1.2–1.5 from operating basicities of 2.8–3.0.

Examination of the calculated physico-chemical properties of the CaO-SiO₂-FeO slags, shows that this transition corresponds to the region of low effective elasticities discussed above. Therefore it is evident that the elastic forces resulting from silica adsorption in this region are insufficient to support a foam from all but the smallest bubbles (–0.1 mm diameter²³⁾). However, foaming may occur in these basic slags as a result of the

Fig. 13. The residence times of 2 mm diameter gas bubbles in foams generated from CaO-SiO₂-FeO slags at 1823 K. Oscillation frequency: 1000 Hz, Elasticity calculated from the data of Kidd and Gaskell⁹⁾ for the surface tension of FeO.

Fig. 14. The residence times of 1 mm diameter gas bubbles in foams generated from CaO-SiO₂-FeO slags at 1823 K. Oscillation frequency: 1000 Hz, Elasticity calculated from the data of Kidd and Gaskell⁹⁾ for the surface tension of FeO.

adsorption of another surface active species, for example, P₂O₅.

From the practical point of view it is preferable to translate the model for the gas residence time to a model that predicts the increase in the height of slag resulting from foaming. The linear model of Bikerman²⁸⁾ which relates the height of foam (H) in the system to the superficial gas velocity (V_g) and the gas residence time (Σ):

$$H = \Sigma V_g \quad \text{.....(16)}$$

can be used for this purpose. It is clear that the foam height is directly dependent on the gas flux, but, in contrast, the gas residence time is independent of the gas flux. As can be seen in Eq. (1), the gas residence time (Σ) is determined by physicochemical properties of

slag of interest and the bubble diameter. In practical iron and steelmaking processes where the gas flux is high, bubbles should be spherical,³¹⁾ and hence Eq. (1) can still be used to calculate the foam height provided that Eq. (17) is valid.

4. Comparison with Slag Foaming Investigations

Zhang and Fruehan²⁵⁾ have developed the following relationship between the gas residence times and the physico-chemical properties of the slag and gas bubble size from the results of laboratory scale slag foaming studies:

$$\Sigma = 115 \frac{\mu^{1.2}}{\sigma^{0.2} \rho d^{0.9}} \quad \text{.....(17)}$$

Clearly, this relationship differs significantly from that developed in the present study to calculate the residence times of gas bubbles in slag foams—Eq. (1). It has already been discussed previously³⁾ that, with regard to the effect of the adsorption of surface active species on foaming, the property of interest is the dynamic, effective elasticity and not the equilibrium surface tension as used in Eq. (17).

The present model (Eq. (1)) predicts that the gas residence time is inversely proportional to the cube of the mean bubble diameter. However, Eq. (17) depicts an approximately inverse relationship between the gas residence time and mean bubble diameter. This is a very surprising result when it is considered that, while the residence time of 2 mm diameter bubbles in a 95 wt% AR grade glycerol solution with a surface tension depression of 10 mN/m is almost 5000 sec, the residence times of 5–10 mm diameter bubbles into the same solution are less than one second.²⁾

An important difference between the cold model and high temperature investigations is that the slag foaming studies were conducted in relatively small diameter crucibles of 30–40 mm diameter compared to the 107 mm diameter column used in the present study.²⁾ To examine the influence of column diameter on foaming, experiments were conducted in a 38 mm diameter column using a 95 wt% glycerol solution with a surface tension depression of 10 mN/m.²³⁾ These experiments showed that 5 mm diameter bubbles produced a polyhedral type foam, consisting of relatively thick films, and essentially identical to slag foams observed in X-ray and optical photographs²⁶⁾ in a 38 mm diameter column but not in the larger 107 mm diameter. Therefore it is reasonable to conclude that wall effects can have a significant influence on foam heights generated from large bubbles in relatively small diameter columns.

Furthermore, the gas residence times for foams generated by slag-metal reactions may be under-estimated in the study of Zhang and Fruehan²⁵⁾ due to non-steady state conditions. Also, for the finest bubbles of 0.7 mm diameter, a gas fraction of 80–90% is obtained if it is assumed that the slag is fully foamed. This suggests that the maximum height of this foam may be constrained by the volume of slag available for foaming. However, repetition of these experiments with increasing slag

masses in order to determine the effect of slag availability on foam heights is hindered by the size of hot zones available in laboratory scale furnaces.

Clearly, Eq. (17) may be considered to contain some uncertainties due to a combination of wall effects for large bubbles resulting in an over-estimation of gas residence times, and non-steady-state conditions resulting in an under-estimation of the residence times of small bubbles, together with the use of the equilibrium surface tension for accounting for the influence of surface active species.

5. Oscillation Frequency in Slag Foams

The oscillation frequency can be determined from the effective elasticity, providing data is available on all the other properties in Eq. (1). Whilst the study of Zhang and Fruehan²⁵⁾ provides this data for mean bubble sizes in the range 0.7–5.4 mm diameter, it has been shown above that the measured residence times in that study are affected by wall effects for large bubbles and non-steady state conditions for small bubbles.

Nonetheless, if it is assumed for the moment that the measured residence time for intermediate sized, 1.7 mm diameter bubbles,²⁵⁾ is reasonably close to the steady-state value, then the oscillation frequency can at least be estimated. The assumption is based on the unproven premise that this bubble size is sufficiently small for wall effects not to be significant but not so small that the foam heights measured by Zhang and Fruehan are far below the steady-state values or limited by the quantity of slag available for foaming.

Using the data of Zhang and Fruehan for the density and viscosity of the CaO–SiO₂–Al₂O₃–FeO slag (3030 kg/m³ and 1.24 Pa·s respectively), the effective elasticity of 1.7 mm diameter bubbles which have a residence time of 25 sec in the foam²⁵⁾ has been calculated to be 8.75×10^{-5} N/m. If it is considered that the activity of silica in this slag is approximately 0.3, the oscillation frequency required to generate this elasticity can be determined from the frequency model.²³⁾ The required oscillation frequency is 16.5–17.8 kHz depending on whether the effective elasticity is determined from Eq. (7) or (8).

As discussed above, the effective elasticity is proportional to the square root of the oscillation frequency. Therefore the effective elasticities and gas residence times in the CaO–SiO₂–FeO slag foams examined in the present study are approximately four times those shown in Figs. 10 and 12–14 for an oscillation frequency of 1 kHz. Under these circumstances the calculated gas residence times of 0.5–2 sec in foams generated in CaO–SiO₂–Al₂O₃–MgO slags in a 1 t smelting reduction vessel²⁷⁾ compare favourably with those for bubbles approximately 2 mm diameter. Unfortunately, the bubble size was not measured in the 1 t smelting tests.

The residence times calculated from the present model (Eq. (1)) for the other mean bubbles sizes generated by Zhang and Fruehan²⁵⁾ are summarised in **Table 1** together with the measured values. In agreement with the arguments above, the residence times of the fine

Table 1. Measured²⁵⁾ and calculated residence times for a range of bubble sizes.

Average bubble diameter (mm)	Measured residence time (Zhang and Fruehan ²⁵⁾) (s)	Residence time calculated from Eq. (1) (s)
0.7	56	358
1.7	25	25
3.0	7.5	4.5
5.1	5.7	0.9
5.4	5.75	0.8

bubbles calculated from the present model are significantly higher than the measured values, while calculated residence times of bubbles greater than 5 mm diameter of less than one second have been shown to be indicative of non-foaming dispersions in the cold model study.^{2,23)}

The present model predicts a gas residence time of 358 sec for the 0.7 mm diameter bubbles, and this would result in a foam height of 1 m at a superficial gas velocity of 2.86 mm/s.²⁵⁾ Assuming that the foam has a gas fraction of 80 %, then it is evident that a minimum slag height of 0.2 m is required to prevent the foam height being limited by the depth of slag available for foaming. Obviously slag and foam heights of this magnitude cannot be contained in a laboratory scale furnace.

6. Conclusions

The application of the current, dynamic model of foaming to foaming of CaO–SiO₂–FeO slags at 1823 K results in predictions that are in agreement with industrial slag foaming investigations. Specifically, the model shows a transition from a foaming to non-foaming regime as the basicity and iron oxide content of the slag increases. The transition is due to low surface elasticities resulting from the negligible adsorption of silica in this region. Within the foaming region, the gas residence times are highly dependent on the gas bubble size, with the gas residence times inversely proportional to the cube of the bubble diameter.

The present model differs significantly from slag foaming models derived from laboratory scale high temperature studies, especially with regard to the influence of gas bubble size. It has been shown that this discrepancy may result from the limitations of conducting high temperature foaming studies, specifically: wall effects resulting from the interactions between relatively large bubbles and the walls of small diameter crucibles; and non-steady-state conditions for foams evolved by chemical reactions. Furthermore, the maximum foam heights may be limited by the depth of slag available for foaming in laboratory scale studies.

REFERENCES

- 1) S. Hara and K. Ogino: *ISIJ Int.*, **32** (1992), 81.
- 2) S. S. Ghag, P. C. Hayes and H.-G. Lee: *ISIJ Int.*, **38** (1998), 1201.
- 3) S. S. Ghag, P. C. Hayes and H.-G. Lee: *ISIJ Int.*, **38** (1998), 1208.
- 4) C. Nexhip, S. Jahanshahi and S. Sun: 2nd Australian Melt Chem.

- Symp., GK Williams CRC for Extractive Metallurgy, University of Melbourne, Australia, (1995), 111.
- 5) Y. Kawai and Y. Shiraishi: Handbook of Physico-chemical Properties at High Temperature, ISIJ, Tokyo, (1988).
 - 6) T. Timucin and A. E. Morris: *Metall. Trans.*, **1** (1970), 3193.
 - 7) K. C. Mills and B. J. Keene: *Int. Mater. Rev.*, **32** (1987), 105.
 - 8) G. Urbain: *Steel Res.*, **58** (1985), 111.
 - 9) M. Kidd and D. R. Gaskell: *Metall. Trans. B*, **17B** (1986), 771.
 - 10) C. F. Cooper and J. A. Kitchener: *J. Iron. Steel Inst.*, **193** (1959), 48.
 - 11) K. Gunji and T. Dan: *Trans. Iron Steel Inst. Jpn.*, **14** (1974), 162.
 - 12) P. Kozakevitch: *Rev. Metall.*, **46** (1949), 505.
 - 13) Y. Kawai, K. Mori, H. Shiraishi and N. Yamada: *Tetsu-to-Hagané*, **62** (1976), 53.
 - 14) T. B. King: *J. Soc. Glass Tech.*, **35** (1951), 241.
 - 15) A. Scheludko: Colloid Chemistry, Elsevier, London, (1966).
 - 16) G. R. Belton: *Metall. Trans. B*, **7B** (1976), 35.
 - 17) J. W. Belton and M. G. Evans: *Trans. Farad. Soc.*, **41** (1945), 1.
 - 18) E. H. Lucassen-Reynders and M. van den Tempel: Proc. IVth Int. Cong. Surface Active Substances, 2, (1964), 779.
 - 19) R. Miller, P. Joos and V. Fainerman: *Adv. Colloid Interface Sci.*, **49** (1994), 249.
 - 20) H. Keller and K. Schwerdtfeger: *Metall. Trans. B*, **10B** (1979), 551.
 - 21) R. F. Johnston, R. A. Stark and J. Taylor: *Ironmaking Steelmaking*, **1** (1974), 220.
 - 22) C. J. Geankoplis: Mass transport phenomena, Holt, Rinehart and Winston, New York, (1972).
 - 23) S. S. Ghang: PhD Thesis, Department of Mining and Metallurgical Engineering, University of Queensland, Australia, (1996).
 - 24) E. Cocchiarella, E. Greenfield and S. Chubbs: *CIM Bull.*, **86** (1993), 56.
 - 25) Y. Zhang and R. J. Fruehan: *Metall. Mater. Trans. B*, **26B** (1995), v803.
 - 26) M. Amatatsu: Report from the Interfacial Transport Phenomena Committee, ISIJ, Tokyo, (1989), 9.
 - 27) Y. Ogawa, H. Katayama, H. Hirata, N. Tokumitsu and M. Yamauchi: *ISIJ Int.*, **32** (1992), 87.
 - 28) J. J. Bikerman: *Trans. Farad. Soc.*, **34** (1938), 634.
 - 29) P. Hrma: *J. Colloid Interface Sci.*, **134** (1990), 161.
 - 30) A. Paul, B. Deo and N. Sathyamurthy: *Steel Res.*, **65** (1994), 414.
 - 31) S. Hartland and A. D. Barber: *Trans. Inst. Chem. Eng.*, **52** (1974), 43.