

Treatment of Transient Phenomena in Analysis of Slag-Metal-Gas Reaction Kinetics

F. Ji, M. Rhamdhani, Subagyo, M. Barati, K.S. Coley, G.A. Brooks,
G. A Irons and S. Nightingale⁺

*Steel Research Centre, Department of Materials Science and Engineering
McMaster University, Hamilton, Ontario, Canada*

⁺*University of Wollongong, New South Wales, Australia*

ABSTRACT

Equations commonly used in describing reaction kinetics are examined and the problem of applying such equations to transient processes is discussed. Three examples of transient phenomena are examined in detail. It is shown that for carbon injection into slag, the reaction can be described by employing data for carbon oxidation in CO/CO₂ by assuming reaction conditions approximately halfway between those in equilibrium with the slag and those in equilibrium with carbon. It is demonstrated that, when the time averaged interfacial area is employed, the rate of reaction between slag and iron-aluminum alloys can be described by a single first order rate equation, accommodating a 300% change in interfacial area. Creation of surface area in oxygen steelmaking is discussed and a method to determine the size distribution of droplets that are generated is proposed. It is concluded that changes in conditions during reaction complicate the analysis of kinetics. However, it should be possible to develop quantitative kinetic models to describe real processes.

1. INTRODUCTION

The authors of this paper consider it a great honour to have been asked to contribute to this celebration of the career of Ken Mills. Ken has contributed extensively to the literature on the physical properties of slags, but there is another theme that runs through his work, that of relevance. Ken is one of the pioneers of mould flux

research /1,2,3/ that has given the world steel industry the level of control in casting that it enjoys today. It is in keeping with this theme, of the application of fundamental data to real problems, that we offer the present paper.

Whilst kinetics remains an exciting academic area, our limited knowledge of a number of factors prevents us from applying lab data to the plant. In fact, one expert in kinetic modeling has stated that the optimism of a previous generation was misplaced and that models of this type will be limited to providing qualitative information on the effect of changing parameters /4/. The current authors, whilst accepting that this is true today, wish to challenge this belief for tomorrow, and offer some suggestions as to the way forward.

If we examine the general rate equation that we use to describe metallurgical reactions:

$$R = k \frac{A}{V} \Delta C \quad (1)$$

This equation assumes mass transport control: similar equations can be written for chemical reaction control, and depending on which phase is controlling the integrated form of this equation takes different forms /5/.

The major problem with the general applicability of Eq. 1 is the assumption that k , A/V and ΔC are constant with respect to time and reaction site. Laboratory studies /5/ have demonstrated that multiple reaction sites can exist when a slag metal reaction occurs in a crucible. The nature of these sites makes it inconceivable that the rate constant is the same for each site.

In general, workers assume that either one site dominates, or that the different sites are "additive", allowing one value to be assumed for "k". However, the relative importance of the different sites is unlikely to be the same in the plant and the lab, therefore scaling-up is not just as simple as it might appear.

In BOF steelmaking, for example, a large number of droplets are emulsified into the metal, resulting in a great increase in reacting surface area. The surface to volume ratio changes with time and blowing conditions, and the value of k, and for that matter ΔC will be different in the case of droplets and the bulk metal bath. These parameters will also be different from droplet to droplet depending on diameter. The issue of emulsification has also been proposed to affect laboratory experiments /6/ creating difficulty in determining a "true" value of k.

It is clear that Eq. 1 is too simplistic to provide a comprehensive description of reaction kinetics. In particular, it is unlikely that such an equation will allow scale-up to the industrial level. A more generally applicable form of this equation which sums all the reaction sites is expressed as follows:

$$R = \sum_i k \frac{A}{V} \Delta C \quad (2)$$

In Eq. 2, no assumptions should be made about the constancy of any of the terms and in order to apply this equation we must have a full understanding of the way in which the terms change with time and process conditions. It should be noted that many successful studies have been conducted using the simplifying assumptions implied in Eq. 1. However, in order to expand the utility of kinetics in industry beyond the merely descriptive, the authors propose the more complete form of the equation expressed in Eq. 2. It is clear that simplifying assumptions must continue to be made, but with the currently available computing power, it should be possible to examine the transient nature of reactions more rigorously. The following examines three aspects of research conducted in our own laboratory, to illustrate ways in which this transience can be treated.

2. INJECTION OF COAL INTO SLAGS

In order to optimize the process of slag foaming in EAF steelmaking, in terms of foaming as well as carbon and iron yield, a comprehensive understanding of the reaction kinetics is required. The reactions between carbon and slag involve three separate steps: FeO transfer from the bulk phase to the interface of slag-gas, CO (C) reacts with FeO at the slag-gas interface, the reaction product, CO₂, transfers through the gas phase to the surface of carbon and CO₂ reacts with carbon to form CO. Those processes involve gas-liquid, gas-solid, even solid-liquid reactions. The gas generated in slag leads to a large number of bubbles being formed in the slag, which results in slag foaming. To understand those phenomena, a number of authors have studied the reactions of FeO reduction in slags thermodynamically and kinetically /7-11/. For the reaction between carbon and CO+CO₂ gas mixtures, Turkdogan gives a detailed description of the reaction rate for different carbonaceous materials /13-16/. In the present work, the overall reaction kinetics of the carbon-slag reaction has been measured, and one approach to a theoretical analysis of the data will be discussed.

2.1. Experimental Procedure

Experiments were carried out by injecting coal into molten slag. The reaction was followed by taking gas and slag samples. Gas analysis was carried out using gas chromatography allowing carbon gasification rate to be determined. Full details of the experimental setup can be found elsewhere /17/.

2.2. Results and Discussion

The activity of iron oxide and slag viscosity and surface tension were estimated using appropriate methods /16, 18/. These properties are shown in **Table 1**. Dust was collected from an in-line filter to determine the amount of carbon lost to exhaust gas; however very little carbon was found. Therefore all carbon that is not oxidized can be assumed to be retained in the slag.

Table 1
Slag chemistry and physical properties.

Exp. No.	Chemical Compositions					Dust		a_{FeO}	μ Pa·s	σ N·m
	Al ₂ O ₃	CaO	FeO	MgO	SiO ₂	W, g	% C			
Inj 4	6.5	56.5	15.0	9.0	13.0	2.69	12.90	0.151	0.119	2730

Figs. 1 and 2 show the outlet gas flow rate calculated according to the analysis of the gas for injections number 4 and 5. The gas flow rate is much higher in injection 4 than in injection 5, because the solid rate in injection 4 was more than double that in injection 5.

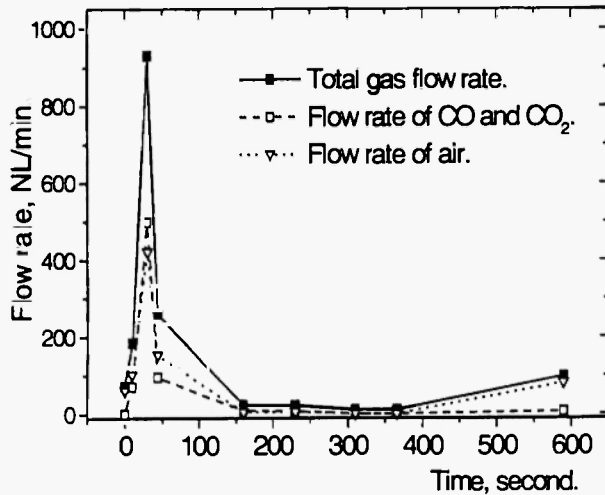


Fig. 1: Gas flow rate for the injection No. 4.

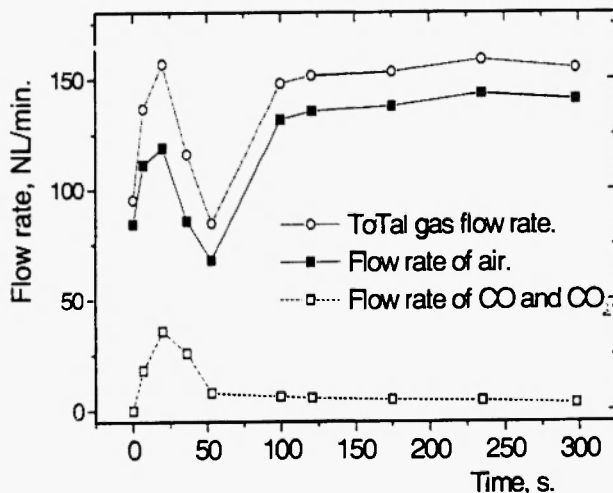


Fig. 2: Gas flow rate for the injection No. 5.

The accumulation rate of carbon in slag equals the rate of injected carbon minus the rate of carbon combustion. During coal injection, i.e. when $0 < t < t_i$, $R_i > 0$:

$$\frac{dw}{dt} = R_i - kw \tag{3}$$

where, w is the amount of coal injected in gram, t is time in second, R_i the injection rate of carbon and k is the apparent first order rate constant of carbon reacted with a CO-CO₂ mixture. Integrating the above equation yields:

$$w = \frac{R_i}{k} (1 - e^{-kt}) \tag{4}$$

After carbon injection stops, i.e. $t_i \leq t \leq t_o$ and $R_i = 0$, the accumulation rate of carbon in slag is:

$$w = w_i \cdot e^{k(t_i - t)} \tag{5}$$

where t_i is injection time and w_i the wt of coal in the slag at $t=t_i$. k is a rate constant for carbon reacting in CO-CO₂ gas mixtures. According to Turkdogan [16], k can be calculated by:

$$k = \frac{\Phi [P_{CO_2} - (P_{CO_2})_e]}{(1 - P_{CO}) / \phi_{CO}}, \text{ min}^{-1} \tag{6}$$

where P_{CO_2} , P_{CO} are partial pressure of CO₂ and CO in the gas phase respectively. P_{CO_2e} is the equilibrium partial of CO₂ in the reaction $CO_2 + C = 2CO$. Φ is a rate parameter which depends on the type of carbon and temperature. The partial pressure of CO₂ is dictated by the equilibration at the gas-slag interface as long as carbon gasification is the rate determining step. If there

is an element of control by the slag/gas reaction we must use a value for P_{CO_2} between that in equilibrium with carbon and that in equilibrium with the slag. The P_{CO_2} and $P_{CO_2c}=3.91 \times 10^{-5}$ atm. were determined using data from reference /13/. Fig. 3 shows the accumulated residual carbon in the slag, predicted using Eqs. 4 and 5, and that determined by gas analysis. It shows that, for the coal employed in this study, the reaction rate with slag can be described reasonably well by Turkdogan's rate expression for metallurgical coke assuming a P_{CO_2} approximately halfway between that in equilibrium with the slag and that in equilibrium with carbon. This result shows that the rate of reaction is controlled by a mixture of reaction at the slag/gas interface and carbon gasification. Further work on a wider range of slag composition and different coals will be required to develop a more generally applicable model.

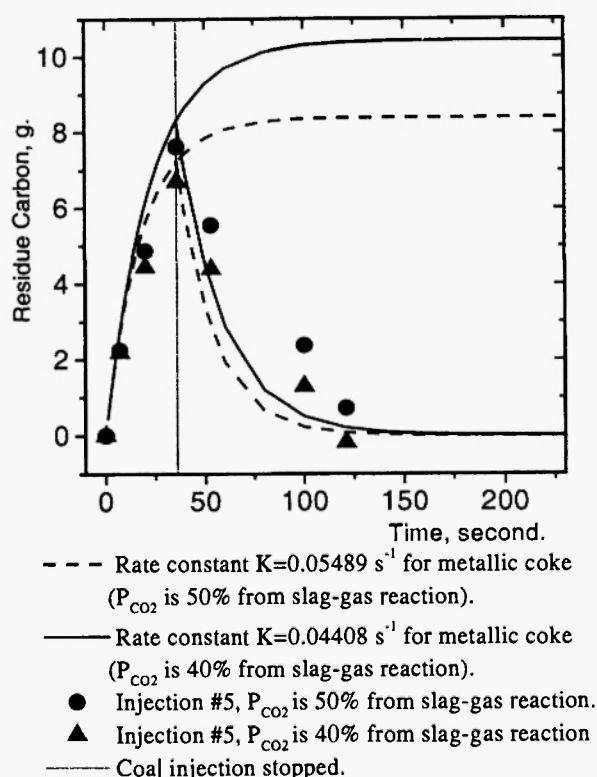


Fig. 3: Comparison of predicted and experimental residual carbon.

3. DROPLET EMULSIFICATION

It is well established that the changes in apparent

interfacial tension caused by high rates of mass transfer can lead to changes in the specific area of the reacting interface. This creates difficulties in ascribing a reaction rate constant to a given system under a given set of conditions.

Riboud and Lucas /21/ conducted extensive experiments to study the influence of mass transfer on surface phenomena. Liquid metal, iron-aluminum system, and liquid slag ($CaO-SiO_2-Al_2O_3$) were heated at the same temperature of $1600^\circ C$ and brought into contact. The change of the shape of the droplet was photographed by x-ray. Interfacial tension measurements were conducted by studying the shape of the sessile metal droplet in the slag. Chung and Cramb /22, 23/ continued the study of dynamic interfacial phenomena on the iron-aluminum system. The droplet dynamic phenomena were noticed for aluminum contents as low as 0.25wt%. Spontaneous emulsification was observed only for systems containing aluminum greater than 3%.

For iron and aluminum alloys reacting with slags, changes in droplet shape have been observed and the dynamic interfacial tensions have been measured. However, only Ooi *et al.* /24/ and Riboud and Lucas included kinetics discussions in their studies. Riboud and Lucas found, that interfacial forces seem to disappear when the oxygen flux is larger than $0.1 \text{ g atom m}^{-2}\text{s}^{-1}$ recovering again when the flux drops to lower than 0.01. Young *et al.* /25/ duplicated the experiments of Riboud and Lucas with the aim of quantifying how the interfacial area varies with instantaneous reaction rate. The current work seeks to analyze the data of Young *et al.*, in conjunction with that of Riboud and Lucas, to develop a procedure to include instantaneous surface area in the quantitative description of reaction kinetics. A limited number of additional experiments were conducted to extend the data of Young *et al.*

3.1. Results and Discussion

Fig. 4 shows that up until 9 minutes of reaction, there was very little reaction interface, one droplet. After 10 minutes the droplet broke up into 28 droplets interfacial area exceeded 1200 mm^2 and significantly affected the kinetics of the reaction. As the reaction proceeded droplets re-coalesced.

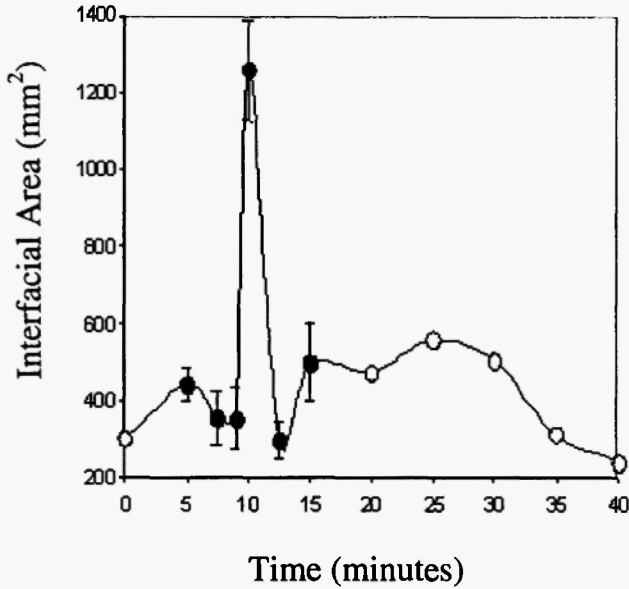
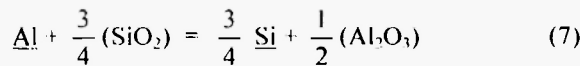


Fig. 4: Interfacial area changes during the reaction of a Fe-4.5%Al droplet with CaO-SiO₂-Al₂O₃ slag; ○-data from Young *et al.* (2000), ●-new data added.

3.2. Kinetics in the Presence of Spontaneous Emulsification

To analyze the reaction kinetics, the authors used the aluminum concentration data from Riboud and Lucas, combined with the interfacial area data from Fig. 4. For the reduction reaction of silica by aluminum in the metal:



Case I:

Employing equation 1 assuming a constant interfacial area, the kinetics can be described by:

$$\ln \frac{[\% Al]}{[\% Al]_0} = - \frac{k \cdot S}{V} t \quad (8)$$

where [% Al]₀ and [% Al] are the initial aluminum concentration and concentration at time t (wt%).

A plot of $\ln \frac{[\% Al]}{[\% Al]_0}$ versus time is shown in Fig. 5.

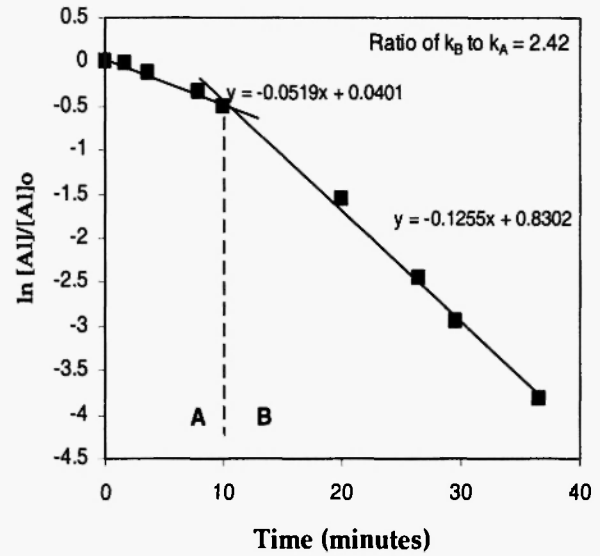


Fig. 5: Plot of aluminum concentration vs. time for case I; interfacial area assumed to be constant during reaction.

The change of slope after 10 minutes of reaction is associated with a sudden increase in surface area due to droplet break-up. Eq. 8 is inadequate because of the assumed constant interfacial area.

Case II:

As Eq. 8 is a time integrated form, we must account for surface area on a time integrated basis as shown in Eq. 9. For simplicity in this case a time averaged surface area was employed calculated according to Eq. 10.

$$\ln \frac{[\% Al]}{[\% Al]_0} = - \frac{k}{V} \cdot \int_0^t S(t) dt = - \frac{k}{V} \cdot F(t) \quad (9)$$

$$\bar{S}(t) = \frac{1}{t} \cdot \int_0^t S(t) \cdot dt \quad (10)$$

Fig. 6 shows the data from Fig. 5 replotted substituting $\bar{S}(t)$ for S. The fit of the data to a single straight line is quite remarkable. The calculated rate constant is $11.3 \cdot 10^{-5}$ cm/s. The use of time-averaged-interfacial-area satisfactorily describes the kinetics of this particular slag-metal reaction where the interfacial area changes during reaction. However, further

experiments are required to validate the general applicability of the approach. A deeper understanding of the change in interfacial area during reaction is needed, before such an approach can be used predicatively.

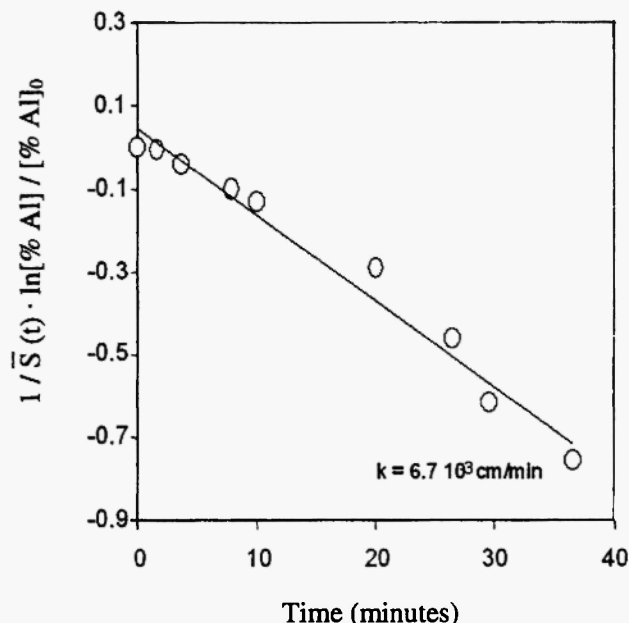


Fig. 6: Plot of case II, a first order reaction with respect to aluminum, time-average-interfacial-areas are used.

4. SURFACE AREA GENERATION IN OXYGEN STEELMAKING

In the foregoing discussion, we have considered ways of handling transient kinetics in the laboratory. In the case of top blown oxygen steelmaking, where intense stirring is used to both enhance mass transfer and create a large interfacial area, it becomes difficult to precisely determine how much interfacial area there is at any one time. Of course, without a good understanding of interfacial area, it is difficult to quantify the overall kinetics of the system.

In oxygen steelmaking, it is commonly accepted that the interfacial area of the metal-slag-gas emulsion is very large compared to the area at the "flat bath" interface and the impact area of the oxygen (the "hot spot"). There have been a number of studies of interfacial area in oxygen steelmaking /26-29/. Meyer *et*

al. /30/ estimated that the total interfacial area in the emulsion fell in the range of 190 to 250 m²/tonne, though Schoop *et al.* /31/ proposed that the area fell in a much lower range, 8 to 12.5 m²/tonne. Part of this confusion stems from having an imperfect understanding of the size of droplets and the amount of metal in the emulsion. If we assume that all droplets are one size and spherical, if the droplet size is decreased from 7 mm to 0.5 mm for a constant 5 % metal in the emulsion, the interfacial area increases 14 times; furthermore, if the fraction metal is increased from 5 % to 30 % for a constant droplet size of 7 mm the interfacial area increases 6 times.

There are some serious practical difficulties in determining the droplet size range in oxygen steelmaking. There is also the complication that the size distribution of droplets generated by the impact of the jet will be different from the size distribution sampled because residence varies widely with droplet size. In general, the reported values of droplet size are measured from droplets recovered from the emulsion /26,29/, not directly measured from the generated droplets. To the authors' knowledge, only a few investigators have attempted to measure directly the size of generated droplets by means of high temperature experiments /29/ and water model experiment /32/. The overall rate of reaction is a function of all of the droplets generated, not just those with long residence times that we can conveniently recover. Plant data indicates that the size of droplets in the emulsion generally lies between 0.05 to 5.0 mm /26/, while high temperature laboratory measurements give the droplet size between 0.04 to 70mm /29/.

As reported by Koria and Lange /29, 34/ when slag metal emulsions are generated by an impinging gas jet, the size distribution of the metal droplets follow the Rosin-Rammler-Sperling (RRS) distribution. Applying the RRS distribution function, to the aforementioned data /26, 29/ the values of the Sauter mean diameter, d_{32} , can be calculated. Comparison of the interfacial area determined by using droplet size in emulsion with using the size of generated droplets shows the interfacial area of emulsion droplets is about seven times higher than the interfacial area of generated droplets. Therefore, using a "snap-shot" of droplets sampled from the emulsion will result in an over estimation of reaction

rate. To obtain a reliable reaction rate Eq. 2 must be summed over all the droplets generated and their residence times. Therefore we must find a way to determine a size distribution that includes all the droplets generated.

By assuming a closed system and steady state emulsification, from the principle of mass conservation in the emulsion, the following equation can be derived:

$$Y_{ij} = \frac{\sum_{j=1}^m X_{i,j} \tau_{i,j}}{\sum_{j=1}^m \sum_{i=1}^n X_{i,j} \tau_{i,j}} \tag{11}$$

where $X_{i,j}$ is the weight fraction of generated droplets with diameter of d_i and residence time $\tau_{i,j}$ and $Y_{i,j}$ is the corresponding weight fraction of droplets of the same size in the emulsion. If we assume all droplets in the emulsion have the same trajectory, χ , and they have a constant velocity, equal to the settling velocity given by Stokes law /35/, Eq. 11 can be simplified to give:

$$Y_i = \frac{\frac{X_i}{d_i^2}}{\sum_{i=1}^n \frac{X_i}{d_i^2}} \tag{12}$$

If it is assumed that no droplets striking the lid fall back into the bath, the droplets stuck to the lid may be used as a representation of the size distribution of generated droplets. However, because the size of droplets is a function of sampling position /29/, a correction is needed. Based on experimental data of Koria and Lange, the effect on sampling position on droplet size can be represented by the following equation:

$$d'_0 = \frac{20d'}{\text{Exp} \left[\frac{3H}{Z + H} \right]} \tag{13}$$

where d'_0 is the RRS distribution parameter for the generated droplets, and d' is the RRS distribution of the droplets taken at distance Z from the top of metal bath, and H is the height of metal bath. It should be noted here that the value of distribution exponent of RRS is

independent to sampling position.

High temperature experiments were conducted to provide data to compare the size distribution of droplets actually generated with that of droplets found in the slag/metal emulsion. Cast iron and calcium-aluminate slag contained in a MgO crucible (190 mm I.D., 295 mm height), were melted in 75 kW induction furnace. Typically 16.3 kg of metal and 3.2 kg of slag were used in the experiments. High purity nitrogen gas (99.998% N_2) was blown through a graphite lance (3mm I.D and 25mm O.D), the exit velocity of the gas was varied from 130 m/s to 240 m/s. The furnace was covered with a lid, made from 2.54 cm Duraboard 2600 Fiberfrax®, which was fitted with ports for an injection lance, a thermocouple, a sampling port, and an exhaust. From each experiment, the size distribution was determined for droplets stuck to the lid and for those found in the slag-metal emulsion.

A comparison of the measured size distribution of the droplets in the emulsion and value predicted from those stuck to the lid using Eq. 12 is presented in Fig. 7. As shown in Fig. 7 there is good agreement between the computed and experimental size distribution. An interesting difference between our predictions and the measured results is that the model predicts that quite large droplets should be recovered in the emulsion, which, in fact, was not observed. This deviation between the predicted value and measured data may be due to the assumption that the emulsion is considered as a homogeneous system and the failure to consider

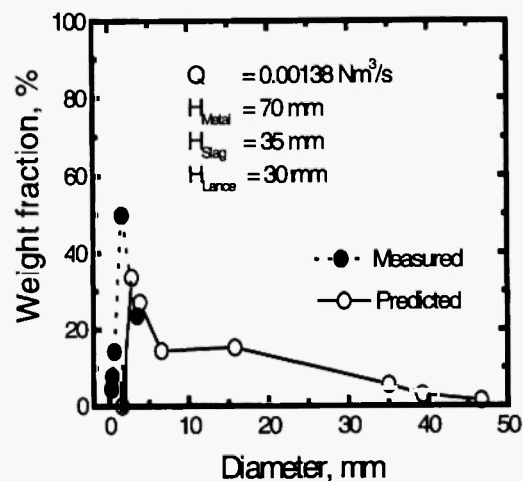


Fig. 7: A typical size distribution of metal droplets in emulsion at steady state condition.

coalescence and break-up of the droplets. As evident from emulsification behaviour in low temperature processes /35-36/, the system is usually non-homogeneous and the coalescence and break-up of the droplets is not negligible. These limitations aside, the results suggest that the procedure developed for calculating droplet size distribution in the emulsion from generated droplet size data is sound. If this procedure is sound, than we should also be able to calculate the droplet generation rate from sampling of the emulsion. This, in turn, should allow us to develop better models for predicting the kinetics of top blown oxygen steelmaking.

5. CONCLUSIONS

- 1) In order to fully describe reaction kinetics in metallurgical processes, the commonly used rate equations must be modified to include the transient nature of the rate constant, surface area and the driving force.
- 2) In the case of carbon injection into slags, the rate of carbon gasification can be described using the available data for the rate of oxidation of carbon. However, the slag gas reaction has an influence on the overall rate and this will only be truly predictive when we have a quantitative understanding of the role of the slag.
- 3) In laboratory experiments dramatic changes in interfacial area can be accommodated in the rate equation, provided we have a detailed knowledge of that area as a function of time.
- 4) There are a number of difficulties in estimating the reacting surface area in oxygen steelmaking; however a method has been proposed to estimate the size and number of droplets generated from samples taken in the plant.
- 5) Our ability to predict the rate of reactions in metallurgical plant is ultimately limited by our ability to account for transient effects. The foregoing discussion has demonstrated that there are ways to treat these effects and that there is considerable scope for work to develop such methods and gather data in support of these methods.

ACKNOWLEDGEMENT

The authors are deeply grateful to Dr. S. Sun, Research and Development of Dofasco for his kindly help on experimental materials and chemical analysis, to O. Kelly, G. Bishop and D. Angelina for great cooperation of the experiments. We would also like to thank researchers at the University of Wollongong, A. Mosbah and L. Brunchurst, for carrying out the surface area measurements on the emulsified droplets.

REFERENCES

1. K. C. Mills, P. Grieveson, A. Olusanya, and S. Bagha: *Proc Continuous Casting '85*, Institute of Metals, London, 57 (1985).
2. R. Taylor and K. C. Mills: *Ironmaking and Steelmaking*, **15**, 187 (1988).
3. K. C. Mills, T. Billany, A. S. Normanton, B. Walker, and P. Grieveson: *Ironmaking and Steelmaking*, **18**, 253 (1991).
4. J. W. Evans: Proc Conf, "Mathematical Modelling of Materials Processing Operations", J. Szekeley, L.B. Hales, H. Henein, N. Jared, K. Rajamani and I. V. Samersekera (Eds.), Metallurgical Society of AIME, Palm Springs, Calif, Nov 29-Dec 2 (1987).
5. R. J. Pomfret and P. Grieveson: *Can Metall Q*, **13**, 287 (1983).
6. S. Simukanga: *PhD Thesis*, University of Strathclyde (1990).
7. H.A. Fine, D. Meyer, D. Janke and H-J. Engell: *Ironmaking and Steelmaking*, **12**, 157 (1985).
8. J. Bygden, D. Sichen and S. Seetharaman: *Steel Research*, **65**, 421 (1994).
9. R. H. Smith and R. J. Fruehan: *Steel Research*, **70**, 283 (1999).
10. Fay Fun: *Metallurgical Transactions*, **1**, 2537 (1970).
11. Jeong-Do Seo and Seon-Hyo Kim: *Steel Research*, **69**, 306 (1998).
12. Sato, G. Aragane, K. Kamihira and S. Yoshimatsu: *Transactions ISIJ*, **27**, 789 (1986).
13. E. T. Turkdogan: *Fundamentals of Steelmaking*, 155.
14. E. T. Turkdogan and J. V. Vinters: *Carbon*, **8**, 39 (1970).

15. E. T. Turkdogan, V. Koump, J. V. Vinters and T.F. Perzak: *Carbon*, **6**, 467 (1968).
16. E. T. Turkdogan and J. V. Vinters: *Carbon*, **7**, 101 (1969).
17. F. Ji, M. Barati, K. S. Coley, and G.A. Irons: *Proceedings of The EAF Conference*, ISS, Nov.10-13, San Antonio, USA.
18. K. C. Mills: *NPL report*, Teddington, Middlesex, TW11 0LW, UK..
19. H. Fujiwara, M. Kitou, T. Matsui and E. Ichise: *Met. Mat.Trans. B*, **30B**, 419 (1999).
20. T. A. Engh, C. J. Simensen and O. Wijk: *Principles of Metal Refining*, Oxford University Press, 85 (1992).
21. P.V. Riboud and L.D. Lucas: *Can. Metall Q.*, **20**, 199 (1981).
22. Y. Chung: *PhD Thesis*, Carnegie-Mellon University, Pittsburgh, PA (1998).
23. Y. Chung and A.W Cramb: *Metall. Trans. B*, **31B**, 957 (2000).
24. H. Ooi, T. Nozaki and H. Yoshii.: *Trans. ISIJ*, **14**, 9 (1974).
25. B.J. Young: *B.Eng Thesis*, University of Wollongong, Australia (2000).
26. Subagyo, G.A. Brooks, and K.S. Coley: *ISS 85th Steelmaking Conference*, ISS, Gaylord Opryland, Nashville, TN, USA, March (2002).
27. B. Deo and R. Boom: *Fundamentals of Steelmaking Metallurgy*, Prentice Hall International, New York (1993).
28. F. Oeters: *Metallurgy of Steelmaking*, Verlag Stahleisen mbH, Düsseldorf (1994).
29. S.C. Koria and K.W. Lange: *Metall. Trans. B*, **15B**, 236 (1984).
30. H.W. Meyer, W.F. Porter, G.C. Smith, and J. Szekely: *JOM*, **20**(7), 35 (1968).
31. J. Schoop, W. Resch, and G. Mahn: *Ironmaking & Steelmaking*, **2**, 72 (1978).
32. N. Standish and Q.L. He: *Transactions ISIJ*, **29**(6), 455 (1989).
33. O.W. Eshbach and M. Souders: *Handbook of Engineering Fundamentals*, 3rd, John Wiley & Sons, New York, 604 (1975).
34. S.C. Koria and K.W. Lange: *Ironmaking & Steelmaking*, **13**(5), 236 (1986).
35. S. Sajjadi, M. Zerfa, and B.W. Brooks: *Dynamic: Chem. Eng. Science*, **57**, 663 (2002).
36. M. Briceno, J.L. Salager, and J. Bertrand: *Trans. IChemE*, **79A**, 943 (2001).

