Progress in the Kinetics of Slag-Metal-Gas Reactions, Past Present and Future

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Abstract: Between the early work on slag metal reactions conducted in the 1950's and the mid 1980s, a generation of metallurgists, contributed much to the theory of slags and their reactions. These workers showed us the importance of charge transfer in slags. They demonstrated that the reaction interface could change dramatically under the influence of reaction and many many questions were asked about the specific reaction mechanisms. This paper will review work in slag metal reactions since the mid 1980s and examine our progress in answering some of the questions raised by the early pioneers. The author will focus on recent work from his own laboratory as well as labs from around the World. Finally the author will make some suggestions regarding future directions in this field.

Key words: Slag-metal Reactions, Kinetics, slag-gas reactions, interfacial phenomena

1. Introduction

The current paper seeks to examine advances in slag-metal-gas kinetics since the 1980s with particular emphasis on more recent work. This does not represent a comprehensive review but more the author's personal view of what has been, and what will continue to be, most interesting and seeks to stimulate debate on these issues. It is recognized that many readers will consider this paper to have ignored what they believe to be most important. The author assures these readers that no slight is intended, but would welcome the possibility that this might promote more active discussion about what is most important in our field. It should also be noted that despite the title of the paper the author has offered little more than a passing nod to all the many great studies on reactions between gasses and liquid metals.

Any review of slag/metal reaction kinetics must include the work of Ramachandran King and Grant[1] These authors showed us that it was important to consider charge transfer in slag/metal reactions and the way in which this leads to coupling between different reactions. They also showed that depending on the relative ease with which particular reactions occur , a system may initially move away from the final equilibrium condition. There continues to be much debate about this work, not its fundamental basis but its implications for arrange of slag/metal reactions.

In 1983 Pomfret Grieveson [2] published a review of work on slag/metal reaction kinetics offering a simple mathematical framework by which slag/metal reactions could be evaluated essentially based on Equation 1

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

Where R represents the rate of reaction k is a mass transfer coefficient or a chemical reaction rate constant delta C is represents the driving force for mass transport or the departure from equilibrium in the case of chemical reaction control. A represents is the area of the reacting interface and V the volume of the phase in which concentration is being measured. These workers analyzed this equation for different boundary conditions and rate determining steps and demonstrated that for a wide range of reactions the rate-determining step is mass transport in the metal phase. This conclusion is now considered a general truth, however, the present author cautions care. When Pomfret and Grieveson published this paper, most kinetic studies of slag/metal reactions had been on systems where the slag/metal partition ratio was high, such as in the case of hot metal desulphurization. One technologically important case where the reaction is not necessarily controlled in the metal is hot metal dephosphorization. In this case the partition ratio is not typically as favourable as for desulphurization and the transport of phosphate species in the slag is likely to be considerably slower than phosphorous in the metal. Consequently, workers have found this reaction to be under mixed control [4] or mass transport in the slag[5] depending on the specific conditions. Pomfret and Grieveson also discussed the mechanisms of a range of reactions, discussing aspects such as gas bubble nucleation and the role of gas phase intermediaries, charge transfer, including the potential role of external conduction through the crucible and the way in which reaction rates might be influenced by other reactions required to balance the charge.

The review by Pomfret and Grieveson could be considered to be a snap-shot of the field of slag –metal kinetics in 1983. Many of the issues raised remain of interest today and although our understanding has improved, there remain many open questions. In addition, most of the work discussed by these authors was based on relatively simple crucible experiments, and whilst these studies offered insight into real processes, there was no suggestion that the results could be applied in the modeling or design of such processes in the way that thermodynamic data from the same era was being applied. The current paper will discuss some of the issues raised by Pomfret and Grieveson and look at how our understanding of the issues has evolved. It will also look at how our ability and desire to use such studies in real processes has evolved and make some suggestions regarding the important questions that must be answered today.

2. The Role of surface Area

A major weakness in employing analysis based on Equation 1, which has been acknowledged for many years, but has also been ignored in many kinetic studies, is that the area of the reaction interface is often neither constant nor known. This issue was demonstrated emphatically by the work of Riboud and Lucas [6] and Gaye et al [7]. These workers showed that during slag metal reactions, the interface will distort because of capillary effects and that under vigorous reactions this may lead to spontaneous emulsification. A number of mechanisms and models have been proposed to explain the increase in surface area during reaction [6-10]. However, we have yet to develop a method to predict the surface area under a given set of reaction conditions.

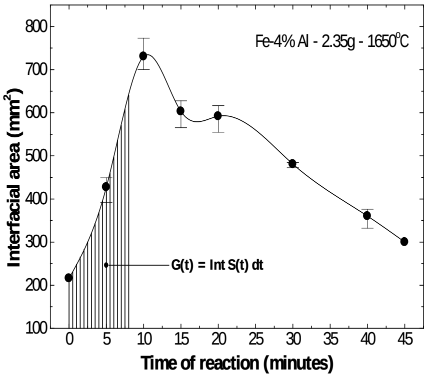

Figure 1: Increase in droplet Surface Area with Reaction Time

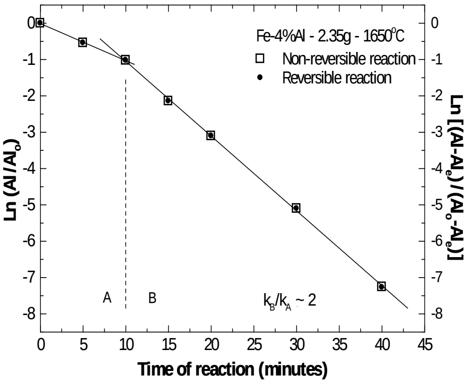

Figure 2: First Order Rate Plot for Al Oxidation from Droplet

Rhamdhani and co workers[11] conducted a set of experiments based on those of Riboud and Lucas. They reacted single Fe-Al droplets with slag and carefully measured the change in surface area as well as chemical composition with time. The latter allowed them to conduct kinetic analysis via a relation similar to Equation 1 the former allowing them to modify this expression to take account of change in surface area. The integrated versions of Equation 1 are given below as Equation 2 and 3. %Al refers to the concentration in the drop at time, t, the subscript,0, refers to time zero, k is the rate constant S is the surface area of the drop and V_m is the volume of the metal drop. S*(t) is the time averaged area calculated according to Equation 4, G(t) is the integral of surface area with respect to reaction time. The results of this analysis are shown in Figures 1, 2 and 3. Comparison of Figures 1 and 2 shows that assuming a constant surface area, results in a sharp break in the rate plot as the droplet surface rises to a maximum. Figure 3 shows the resulting plot when a time averaged surface area is employed. Note it is necessary to use a time averaged area because the rate plot represent the integrated version of the rate equation and as such, each successive data point includes data from all earlier reaction times. This method shows that it is possible to accommodate changes in surface area. However, it does not predict the surface area change.

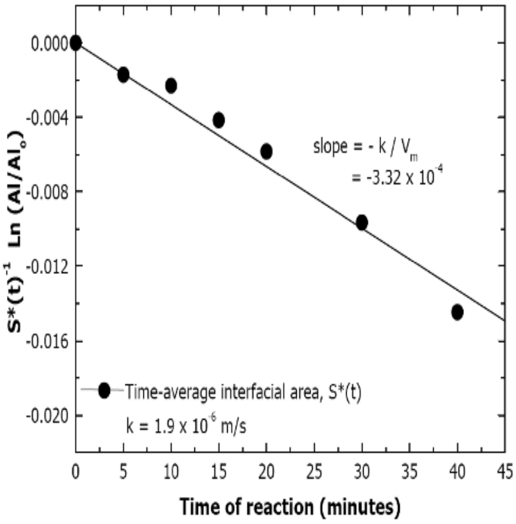

Figure 3 First Order Rate Plot Normalised for Surface Area

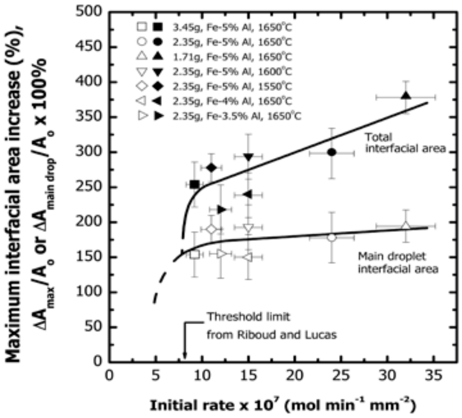

Figure 4 Increase in Area as a Function of Reaction Rate

$$\ln\frac{[\%\,\mathrm{Al}]}{[\%\,\mathrm{Al}]_0} = -\mathrm{k}\frac{\mathrm{S}}{\mathrm{V_m}}\mathrm{t} \qquad (2)$$

$$\frac{1}{\mathrm{S}^*(\mathrm{t})}\ln\frac{[\%\,\mathrm{Al}]}{[\%\,\mathrm{Al}]_0} = -\frac{\mathrm{k}}{\mathrm{V_m}}\mathrm{t} \qquad (3)$$

$$S^*(t) = \frac{1}{t}G(t) = \frac{1}{t}\int_0^t S(t)dt \qquad (4)$$

In another paper Rhamdhani et al [12] also found, in agreement with previous workers[6,7] that the increase in surface area of the reacting drop came from three different sources:

1/ Flattening of the drop

2/ Roughening of the drop surface

3/ Shedding of satellite droplets

These workers showed that at a certain oxygen transfer rate the droplet would change shape and the surface would become rough, this resulted in an increase in the surface area of the parent drop. As the rate of oxygen transfer increased beyond this rate, there was little change in the surface area of the parent drop, however, the overall surface area in the system increased by creating satellite droplets. As is shown in Figure 4. Almost all the increase in surface area after a threshold value is reached, is due to the formation of new droplets. It appears that once the threshold mass transfer rate is achieved, the droplet will distort and roughen to a certain point, at which it becomes energetically favourable to form droplets from the surface protrusions, rather than to increase the level of roughness or further distort the shape of the parent droplet.

Another interesting finding of Rhamdhani, is the relationship between the free energy change and the increase in surface area. Assuming the overall reaction to be as follows:

$$\underline{Al} + \frac{3}{4}SiO_2 = Al_2O_3 + \frac{3}{4}\underline{Si} \qquad \Delta H = -180{,}170\,J/mol \qquad (5)$$

Rhamdhani et al calculated the change of free energy as a function of extent of reaction, ξ. Using Equation 6 it was possible to calculate the free energy change, λ, at the point in the reaction where area is at a maximum..

$$\lambda = \int_0^{t_{A-\max}} \frac{d\Delta G}{d\xi}\frac{d\xi}{dt}dt \qquad (6)$$

The measured maximum change in surface area is plotted in Figure 5, against λ, for a number of different experiments. There is clearly a very strong linear correlation and intuitively the slope of the line in Figure 5, should represent the surface energy of the metal. However, calculation shows that this energy is several orders higher than any reasonable estimate of the surface energy, suggesting that it is not the energy of the surface itself that must be balanced by the reaction but the energy required for the process of creating new surface. Further work is required to elucidate the precise mechanism, however, the concept of balancing the rate of free energy change with surface area generation is consistent with the concept of free energy gradients, employed by Friedel[13] to predict spontaneous emulsification. Another remarkable aspect of the observation of Rhamdhani et al , is the apparent constancy of the relationship across the range of conditions studied. This implies that the same energetic relationship applies to all three mechanisms of surface area generation. If the mechanism for this effect can be explained or even a consistent empirical correlation developed, to predict surface area change in slag/metal systems, the application of laboratory kinetic data to real processes will take a big

3. Gas Phase In slag Metal Reactions

Pomfret and Grieveson[2] considered the role of transport across gas bubbles in the reduction of silica. This was of particular interest because a number of researchers had highlighted the role the diameter of the crucible played in reduction of silica from slags. Pomfret and Grieveson suggested that from analysis of the work of a number of investigators, it appeared that much of the reaction occurred via the transport of SiO gas across an annulus of CO formed at the line of contact between slag/metal and graphite crucible. These workers also considered the reduction of manganese and iron from slag by carbon saturated iron. In both cases they pointed to the effect of CO nucleation and the potential for an annulus of CO to form around the circumference of the crucible. They also discussed stirring by CO causing an autocatalytic effect. In addition they showed that, when a metallic reductant was available, it tended to dominate the reduction until its concentration fell to a level where carbon oxidation was favoured. In fact, they show that silica reduction is three times faster by managanese in the metal than by carbon. This is consistent with the early findings of Ramchandaran King and Grant[1], who showed that metallic elements will transfer during desulphurization in advance of CO formation. Eventually these elements will be reduced via the more thermodynamically favourable reaction with carbon.step forward. This effect is seen in more recent work. Jones [3]showed that sluggishness of CO

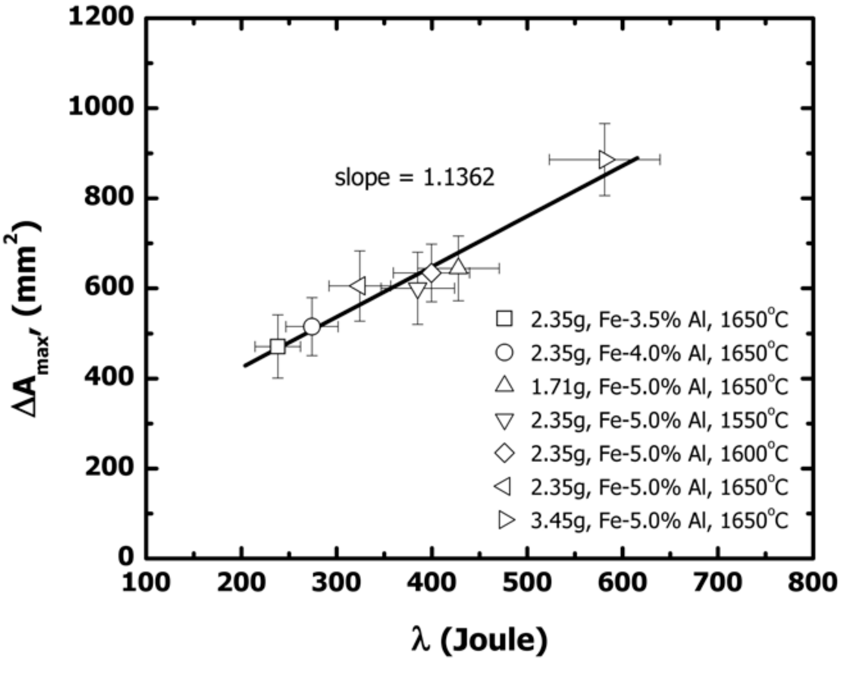

Figure 5 Maximum Increase in Area as a Function of Free Energy Change

nucleation can retard the desulphurization and that the presence of metallic reductants can lead to substantially faster rates. Jones also investigated the idea that the “crucible contact” effect discussed by Pomfret and Grieveson, could be related to the availability of an external path for elctrons to participate in charge balancing. He conducted a range of experiments in graphite crucibles where he used alumina inserts to selectively mask either, the slag, the metal or the slag/metal interface. Whilst his results showed significant differences betwee the various configurations, he was not able to offer conclusive evidence for the role of a conducting path in preference to a preferred nucleation site for CO. It is clear that in many slag metal reactions the nucleation of CO is a critical and often limiting step. The presence of a stable annulus of CO around the crucible wall would be expected to eliminate the need to nucleate on an on going basis, thereby accelerating the reaction.

Not withstanding the discussion above, several researchers have shown, that an external conductive path can have a profound effect on the rate of reaction, in the case where a potential is applied across the slag metal interface. Despite the magnitude of the effect and even the development of technology this concept has not taken off from a technological standpoint and from a research perspective has also gone quiet in recent years.

4. Reduction of Oxides in Slag by Carbon

There has been an extensive body of research on reduction of oxides from slag, because of the widespread application. It is beyond the scope of this paper to offer a comprehensive review on smelting using carbon. Therefore discussion will be confined to a few key publications which in the author’s opinion emphasize important aspects of our current understanding of the field.

Carbon as a reductant is typically added to slag in one of two forms, solid carbon, or carbon dissolved in metal. In both cases, the reaction is assumed to proceed via a gas “halo” formed around the particle or droplet. Since the early work of Mulholland et al[14] , our picture of carbon bearing metal droplets reacting with slag has been of a droplet surrounded by a halo of CO/CO_2, the reaction proceeds via a number of steps: 1/ mass transport of oxide in the sag, 2/ slag/gas reaction; mass transport in the halo, 3/reaction at the gas/metal interface and 4/ mass transport in the metal.

In the case of solid carbon reacting with slag Fruehan et al [15] suggested for higher FeO contents, a mixed control regime involving the slag/gas reaction, transport in the halo and gas/carbon reaction. Story et al[16] suggested that for graphite the rate was typically controlled by the gas/slag reaction and mass transport in the slag. However these workers did suggest that this will be dependent on the carbon and less reactive forms of carbon may well lead to control by the gas carbon reaction. In a recent paper Corbari et al[17] suggested that at higher FeO contents the rate was controlled by a combination of the slag /gas reaction and the gas carbon reaction, where the gas/carbon reaction is under limited mixed control. In another recent publication King et al[18] presented a model for the kinetics of carbon injection into slags. The model was based on the concept of individual carbon particles reacting inside an expanding gas bubble. These workers found that in the early stages of reaction the process was under mixed control involving slag/gas and gas/carbon reactions. As the reaction proceeds and the slag surface area increases, the gas/carbon reaction dominates the rate. This work agrees in general terms with Corbari et al[17] with the exception that King et al assumed complete internal burning of carbon. This can be explained by the fact that King et al used smaller carbon particles.

For the case of iron carbon droplets reacting with slag, Min and Fruehan[19] conducted an analysis of each of the possible rate determining steps and concluded that for high sulphur iron, the reaction was controlled by the metal/ gas reaction because of the retarding effect of sulphur. For low sulphur metal the reaction was controlled by a combination of mass transport in the slag and in the halo. This finding is contrary to the accepted mechanism for reaction with solid cabon, however, these workers calculated that the slag/gas reaction and transport in the metal should be much faster than the other steps. A complicated model was developed by Murthy *et al.*[20, 21] to explore the possibility of gas halo transport control. Indeed it was shown to be feasible that transport in the halo controls the reaction, but it is proposed that because of the frequent collapses of the halo, gas phase transport cannot be the only rate controlling mechanism. In fact, in their suggestion that increased conductivity of the slag would enhance the reaction, these workers imply that mass transport in the slag is rate controlling. Gare and Hazeldean[22] did not propose a rate determining step but defined a number of different “reaction regimes” based on phenomenological observations. These workers also discussed an internal external regime in which the halo was somewhat unstable and gas nucleation inside the droplet occurred. Gaye and Riboud [23] also made similar observations but their emphasis was on the swelling of the droplet at lower carbon contents which these workers termed emulsification.

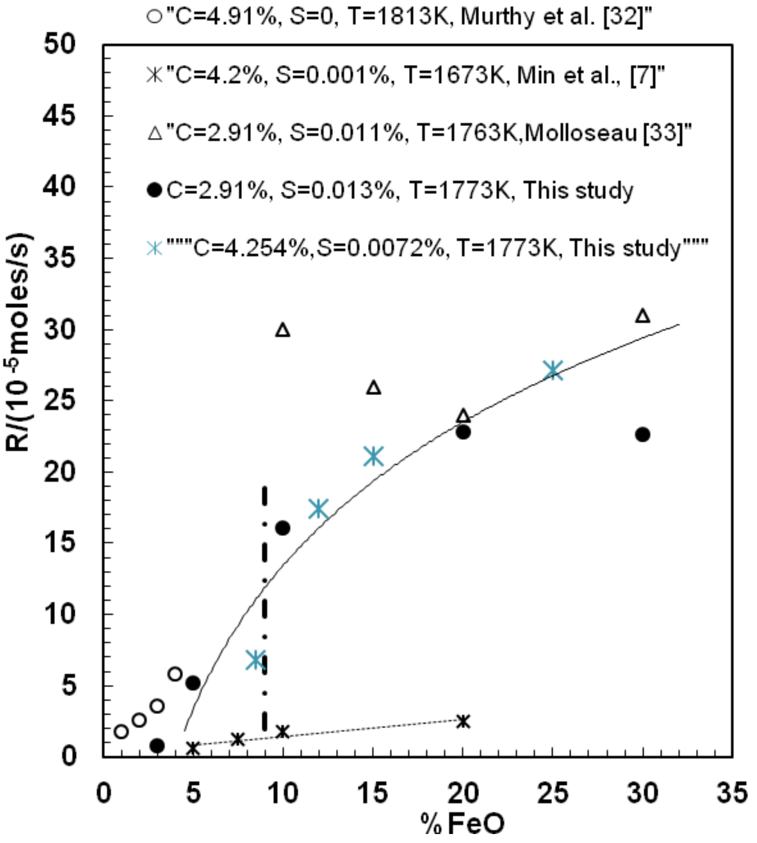

Figure 6: Rate of Gas Evolution from Fe-C Droplets as a Function of FeO

The phenomenon of droplet swelling has since been studied in detail by Molleseau and Fruehan[24] and Chen and Coley[25]. Chen and Coley have developed a model based on nucleation theory which describes the CO generation quite well. Data from these workers is presented in Figure 6 along with that from other researchers who observed halo formation. Pomeroy and Coley [26] have recently published work, which attempts to define the boundary between halo formation (external formation of CO) and swelling (internal gas nucleation). These workers suggest that the regime in which swelling will occur is quite extensive, provided there is sufficient FeO in the slag and some sulphur present to assist the gas nucleation.

The effect of surface active elements on the reduction of Chromium from slags by carbon saturated iron offers some interesting insight into the role of CO formation. Figure 2 shows the concentration of Cr^{3+} in the slag during reaction with carbon saturated iron, as a function of time and metal sulphur content, based on data taken from Simukanga[27]. The rate of reduction increases with increasing sulphur content, a result that is contrary to the very well established view, that sulphur poisons reaction sites. Simukanga explained the apparent contradiction as being caused by slag/metal emulsification; the decrease in interfacial tension caused by increased sulphur, increased the slag/metal interface via emulsification of metal droplets. Simukanga did not have any direct evidence of emulsification but the explanation would seem reasonable, particularly in light of other work on slag /metal emulsification[6,7]. However, in an attempt to verify the proposed mechanism, experiments were conducted in the author's laboratory using x-ray imaging of the slag/metal interface, under conditions identical to those employed by Simukanga; no emulsification was observed.

Recent work[25,28,29] , has shown that the nucleation rate of CO in high carbon droplets, increases with increasing sulphur up to a certain maximum. This has been explained as resulting from the surface active nature of sulphur, decreasing the barrier for nucleation. suggesting another source for the increase in reaction rate. Pomeroy, Brown and Coley [28] employed x-ray fluoroscopy to examine the tendency for swelling at the much lower oxygen potentials employed by Simukanga[27] in his work. They compined this technique with a constant volume pressure increase technique to study the reaction kinetics. They used the following slag composition which is exactly the same as that used by Simukanga: 42% SiO_2 38% CaO 5% Cr_2O_3 15% Al_2O_3. They also replicated the temperature and employed a range of sulphur contents spanning the range employed by Simukanga. The kinetic data for gas generation rate are shown in Figure 5 as a function of metal sulphur content.

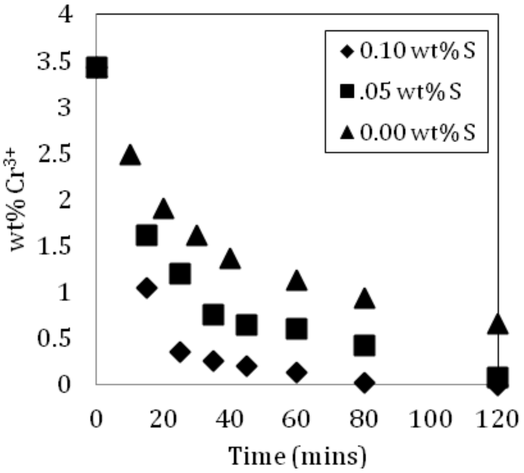

Figure 7: The effect of Sulphur on the Reduction of Cr^{3+} from Slag from Simukanga

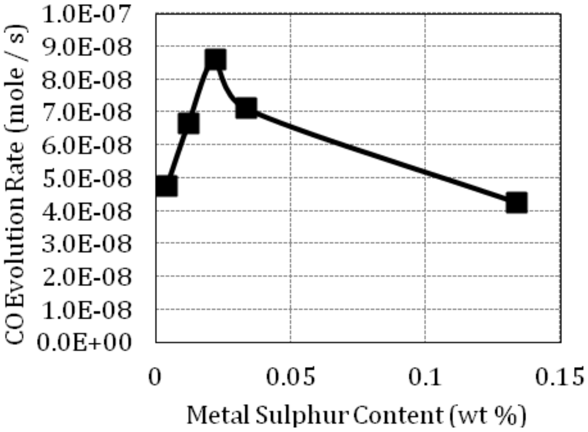

Figure 8: Observed Variation in CO Evolution Rate with Metal Sulphur Content[29]

Coley et al[29] pointed out that slow rates of CO nucleation can be beneficial; in the case of hot metal dephosphorization it has been found that the oxygen potential that drives the reaction lies between that in equilibrium with carbon in the metal and that in equilibrium with FeO in the slag. Figure 9 shows data taken from Monaghan et al oxygen potential is plotted against the Fe^{3+}/Fe^{2+} for two cases; where it assumed to be controlled by FeO in the slag and where it is calculated from the measured phosphorous partition. We can see that the two sets of data coincide. The oxygen potential in equilibiium with carbon in the metal would be several orders of magnitude lower. Wei et al[4] found in gas stirred systems the oxygen potential was lower and at higher rates of stirring moved closer to the CO/C equilibrium. In the case the gas stirred system, CO can form on preexisting gas bubbles.

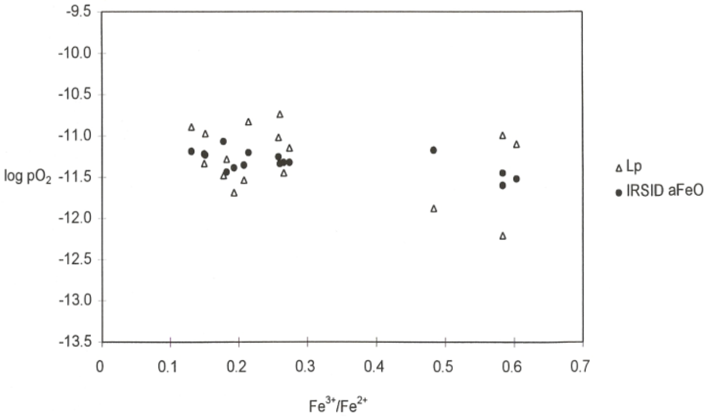

Figure 9: log pO_2 as a function of Fe^{3+}/Fe^{2+} in the slag; triangles determined from experimental phosphorous partition and circles calculated from FeO in slag

5. Gas Slag Reactions

In the foregoing sections there has been some discussion of gas phase “ferrying” particularly in reactions involving carbon oxidation, either from solution in the metal or as carbon particles reacting with the slag. At FeO levels in the slag greater than 20% mass transport in the slag is sufficiently fast and does not normally control the rate. Typically in this case the reaction will be controlled by a mixture slag/gas reaction and gas carbon reaction depending on the relative surface areas of the two interfaces. Because of this many workers have studied the kinetics of slag/gas reactions, in particular the reaction between CO/CO_2 gas mixtures and slag[30-41]. Arguably the most notable contribution in this area was Belton and co-workers[31-34] who pioneered the use of the isotope exchange technique in this field. Building on the work of Belton several other groups over the last 20 years have built a complete picture of the reaction.

$$CO_2(gas) = CO(gas) + O(slag) \qquad (7)$$

The rate, ν, of the above reaction can be represented by Equation 8 where k_a is the apparent rate constant p_i is the partial pressure of species i and a_o represents the activity of oxygen in local equilibrium with the slag where CO_2 /CO= 1 is the standard state.

$$\nu = k_a (p_{CO_2} - p_{CO} a_O) \qquad (8)$$

$$k_a = k_a^0 (a_O)^{-\alpha} \qquad (9)$$

Where k_a^0 and α are both functions of slag basicity and iron oxide content. Many excellent studies have developed a general qualitative understanding of the reaction. However, until relatively recently there has been no quantitative model which is consistent with all experimental observations. Sasaki et al[31] and El-Rahaiby et al[34] found α to be equal to 1 which led to the suggestion the rate determining step involved a doubly charged adsorbed CO_2 complex whereas other workers found lower values[36, 41]. Some workers observed no dependency of k_a^0 on slag FeO content[34] whereas others found a strong dependency[38,41]. Also similar inconsistencies' exist regarding the effect of basicity. Barati and Coley[42], based on detailed analysis of their own extensive data set, developed a model which is able to rationalize all reported observations and shows excellent quantitative agreement with other data reported in the literature. Based on the finding that α=1 early workers assumed that the rate determining step must involve the transfer of 2 electrons, hence the assumption that a doubly charged adsorbed complex was involved[31, 33, 34]. However CO_2^{2-} is not known to exist, whereas the existence of CO_2^- is well established[43,44]. In addition, although the early researches found α to equal unity, the findings of lower values of by other workers could not be satisfactorily explained. Earlier workers had based their findings on the assumption that the value of α is dictated by the charge on the activated complex. On that basis, the only way to justify a value of 1 was to assume CO_2^{2-} was the activated complex. Barati and Coley[42] pointed out that there is also a requirement for available adsorption sites which in this case requires two adjacent ferrous ions. When the effect of a_o on the concentration of sites was taken into account, Barati and Coley showed that if the activated complex was singly charged, α could assume a range of values between 0.5 and 1. These workers also used the mechanism proposed by Sun and Belton[32] to account for the effect of basicity on free electron activity. Combining these approaches they were able to develop the following relation, which they validated for a wide range of data generated by themselves and other workers.

$$k_a = 2.67X10^{-4} (C_{Fe})^2 \frac{1}{r(1+r)^2} \exp\left(\frac{-(475.7-452\Lambda)}{RT}\right) \left[\text{mol.cm}^{-2}.\text{atm}^{-1}\cdot\text{s}^{-1}\right]$$

Where r= Fe^{3+}/Fe^{2+}, C_{Fe} is the concentration of iron in the slag and Λ is the optical basicity of the slag.

6. Practical Application of Kinetics

Since 1983 when Pomfret and Grieveson offered us a snap shot of the state of slag/metal kinetics a lot has changed. However, the biggest change has been in the way kinetic studies are applied, or at least their application is contemplated. As stated in the introduction to this paper, these workers reviewed mostly small crucible single reaction experiments which were aimed at developing mechanistic insight. Almost 30 years later, as evidenced by much of the foregoing, researchers continue to conduct small scale laboratory experiments, seeking insight. However, with the increase in computing power, we can begin to contemplate the application of kinetic data in comprehensive process models. Kitamura[45] has reviewed the importance of kinetic models in steelmaking and suggested that in the past thermodynamic models received more attention but that it might be timely to shift the focus to kinetic models in order to rationalize some of the discrepancies between equilibrium calculations and observed behaviour. He presented case studies on the use of kinetic models for the BOF, for vacuum degassing and for hot-metal dephosphorisation. In all cases these models showed reasonable agreement with plant behaviour. However, these models, whilst based on a mechanistic understanding, are somewhat empirical, and it is the view of the current author that such models would benefit greatly from some detailed and fundamental mechanistic work.

Sukla et al [46]reviewed the literature on kinetics of reactions important in BOF steelmaking and suggested that at least during the main part of the blow, the process could be described based on equilibrium partition of oxygen supplied. However to get good predictions of the features observed in oxygen steelmaking, these authors had to employ a dynamic model, combining their equilibrium model with “efficiency factors” which are related to the kinetics of the individual reactions. Whilst these authors demonstrated some success with this model it would appear that a priori prediction of the efficiency factors requires an understanding of the kinetics of the individual reactions.

Kattenbelt and Roffel[47] developed a model to describe the response of oxygen steelmaking to step changes in process variables such as oxygen blow rate, lance height and oxide additions. These workers used insights obtained from work on droplet generation, size distribution and residence time to define the parameters to be considered in an empirical relation for decarburization rate. However, they did not employ any of the fundamental relations directly. Despite the empirical nature of the relations used, these workers showed excellent agreement between their predictions and measured data from BOF steelmaking.

Recent work by Brooks and coworkers[48,49] has shown the power of combining fundamental work on micro-kinetics with a global process modeling approach. This work has combined several sub-models based on fundamental principles[50, 51], with detailed micro-kinetics studies[24,25] and plant data[52]. From the perspective of a researcher who is focused on micro kinetic studies, it is very exciting to have the opportunity to apply ones work in models that describe what happens at the largest scale.

7. Conclusion

The first three decades of research in slag/metal/gas reaction kinetics presented us with a basis for understanding the field, and asked many questions. Over the last almost three decades, we have continued to build on the work of the early researchers. We have extended the scope of the reactions studied, we have applied more sophisticated techniques and we have re-asked all of the many questions. However, have we answered them? We have developed a much more general understanding, we have accumulated data and we have refined our theories through direct observation. On the other hand, whilst we have accumulated an enormous body of measurements from quantitative experiments, which has helped us develop insights that can be applied in understanding and optimizing processes, we have typically not generated data that can be applied directly in a quantitative manner. The challenge that we must set ourselves for the future is to turn the understanding of the past into real quantitative data backed by theoretical models that are quantitatively predictive. These can then be applied in the global models of processes such as those developed by Brooks and co-workers and Kitamura et al.

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