Fundamental Kinetic Studies of Slag Metal Gas Reactions in Support of Process
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Abstract

High temperature metallurgical reaction kinetics have been the subject of study for many years [1, 2]. However, for most of that time such studies, whilst presenting a stimulating intellectual challenge to academic researchers, have been considered to offer no more than an insight into the behaviour of industrial processes. However, in recent years hope has been expressed, regarding the emergence of kinetics as a discipline with quantitative application, much as thermodynamics has been for several decades [3]. Indeed, there has been notable recent success in process modelling of real plant data, based on a fundamental kinetic approach [4]. The current paper will discuss two fundamental studies from the author’s laboratory and the way in which they have been applied in modelling process behaviour.

Kinetics of Slag Gas Reactions

Carbon injection into slag has been used in smelting reduction and in slag foaming in the electric arc furnace (EAF). To develop a proper model of such a process it is important to understand the mechanism and possible rate determining steps for reaction between individual carbon particles and slag. A number of researchers have suggested that when a carbon particle reacts with oxidising slag, a CO/CO₂ halo forms around the particle [5, 6] requiring individual gas/slag and gas/carbon reactions for reduction to proceed. Given the relatively thin halo and the rapid nature of gas phase mass transport, it is likely that such either the gas/slag, gas/carbon reactions or transport in the slag will be rate determining. It has been reported that for low iron oxide slags the latter controls and for higher iron oxide, one or other of the chemical reactions is rate determining. The gas carbon reaction has been well studied [7] as has the slag gas reaction [8]. However, in the latter case, workers had been previously unable to offer a theoretical explanation that would explain all of the observed phenomena. Barati and Coley [11], employed the isotope exchange technique pioneered in the Metallurgical field by Belton and co-workers [8-10], to develop a data set covering a wide range of slag and gas composition. These workers found, in agreement with previous researchers [8-10], that the rate of reaction could be described by Equation 1 and the apparent rate constant represented by Equation 2.

\[ v = k_a (p_{CO_2} - p_{CO} a_{O}) \]  \hspace{1cm} (1)

\[ k_a = k^o_a (a_{O})^{-n} \] \hspace{1cm} (2)

The value of the parameter n has been found to lie between 0.5 and 1, and it has proved problematic to justify the range of this and effect of basicity and FeO concentration on \( k^o_a \). The primary reason for the discrepancy in n is the assumption that reaction must proceeds via
an adsorbed activated complex of the form (CO$_2$)$_2^2$. This was originally proposed because it fits very well with a value of n = 1, but is contradicted by the fact that (CO$_2$)$_2^2$ is known to be unstable, whereas (CO$_2$) is more stable. Barati and Coley [12] identified that if the reaction proceeds via the singly charged activated complex the reaction site requires two neighbouring Fe$^{2+}$ ions. If this requirement is included in the rate equation, the observed range of values for n can be explained as can all other observations. Based on this mechanism, Barati and Coley [12] developed Equation 3 to calculate the rate constant for reaction between CO/ CO$_2$ and FeO-CaO-SiO$_2$ slag.

$$k_o = 2.67 \times 10^{-4} (C_{Fe})^2 \frac{1}{r(1 + r)^2} \exp \left( \frac{-475.7 - 452.4\Lambda}{RT} \right) \text{ [mol} \cdot \text{cm}^{-2} \cdot \text{atm}^{-1} \cdot \text{s}^{-1}] \quad (3)$$

Where $r = \text{Fe}^{3+}/\text{Fe}^{2+}$, $C_{Fe}$ is the concentration of iron in the slag and $\Lambda$ is the optical basicity of the slag. The agreement between this equation and experimental measurements is excellent over the entire range of slag composition and temperature employed by Barati and Coley.

Combining Equation 3 with the rate equation of Turkdogan and Vintners for carbon gasification allows the calculation of the rate for a single carbon particle surrounded by a gas bubble. King and co-workers [13, 14] integrated the resulting rate equation over all injected particles to predict the rate of carbon gasification during injection. Figure 1 shows the agreement between the model proposed by King et al and measurements of gasification rate. The agreement is very good but as is shown in the figure, by assuming the carbon to be less reactive than that studied by Turkdogan and Vintners (adjusted carbon reactivity), better agreement is obtained. The gasification model can be combined with the foaming model of Zhang and Fruehan [15] to predict slag foam height [13].

Figure 1: Carbon gasification rate as a function of time from King et al. [13, 14]

Droplet Swelling in BOF Steelmaking

Recent work from Swinburne University [4], has shown that BOF steelmaking can be quantitatively modelled with remarkable success, when a deep understanding of the kinetics and mechanisms of the various reactions is employed [4]. In this work Dogan et al [4] used...
the bloated droplet model first proposed by Brooks and co-workers [16] to calculate the residence time of metal droplets in the slag.

To be used over a wide range of conditions the bloated droplet model requires a detailed evaluation of swelling kinetics caused by CO formation inside the droplet. Considerable progress in this regard has been made through recent research by Coley and co-workers [17, 18].

Conclusions

Process models based on detailed kinetic analysis of the key phenomena offer the best opportunity for accurate prediction of process behaviour.

References

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