Rate of Interfacial Reaction between Molten $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_xO$ and $CO\text{-}CO_2$

Y. LI and I.P. RATCHEV

Measurements of the rates of reduction of iron oxide from molten $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_xO$ slags by Ar-CO mixtures have been made using a thermogravimetric method. The apparent first-order rate constant, with respect to the partial pressure of CO, of the gas/slag interfacial reaction was deduced from the measured rates, where the effects of the mass transfer in the gas and slag phases were minimized. It was found that the apparent first-order rate constant decreased with the concentration of 'FeO' from 100 to 20 wt pct, whereas it remained essentially constant in the range from 5 to 20 wt pct 'FeO'. At a given iron oxide concentration, the reduction-rate constant increased significantly with an increase in the CaO/SiO_2 ratio. For fixed slag compositions, the reduction rate increased slightly with the oxidation state of the slags. When the rate constant is expressed in the form of $k = k'(Fe^{3+}/Fe^{2+})^{\alpha}$, the values of α range from 0.15 to 0.25. The effect of temperature in the range from 1673 to 1873 K on the reduction rate of iron oxide in a $40.4CaO\text{-}40.4SiO_2\text{-}14.2Al_2O_3\text{-}5$'FeO' (wt pct) slag was studied. The calculated activation energy, based on these results, is 165 kJ/mol.

I. INTRODUCTION

DRIVEN by the needs in the development of new bath-smelting technology, a great deal of research attention has been given to the reduction of iron oxide in the *liquid state* by solid carbon or carbon dissolved in liquid iron. In the DIOS and AISI processes, for example, the iron oxide dissolves in the slag, and about half of it is reduced by the carbon in iron droplets ejected from the iron bath. The other half of the iron oxide is reduced by coal char. The overall reactions can be expressed as

$$(FeO) + C \text{ (or } \underline{C}) = CO + Fe \qquad [1]$$

They are typical heterogeneous reactions involving iron oxide-containing liquid slag, solid carbon (or liquid metal), and gases. As soon as the reaction is initiated, a gas phase is formed and the direct contact between the slag and solid carbon or liquid metal is blocked. The reaction is then likely to proceed *via* two sequential reactions, with $CO\text{-}CO_2$ acting as gaseous intermediates, *i.e.*,

$$CO + (FeO) = CO_2 + Fe \qquad [2]$$

at the gas/slag interface, and

$$CO_2 + C \text{ (or } \underline{C}) = 2CO \qquad [3]$$

at the gas/carbon or gas/metal interface. The existence of a gas film or halo between an iron oxide–containing slag and the solid carbon or liquid metal has been confirmed by direct observations of the reaction using X-ray fluoroscopy.[1–7] There are several possible rate-controlling processes, plus combination of these in series:

(1) reduction of iron oxide in slags by CO on the gas/slag interface, *i.e.*, Reaction [2];
(2) mass transfer of Fe^{2+} and O^{2-} from the bulk slag to the slag/gas interface;
(3) mass transfer of CO from the gas/carbon interface to the gas/slag interface and of CO_2 from the gas/slag interface to the gas/carbon interface;
(4) reaction of CO_2 and solid carbon or carbon in metal on the gas/solid or gas/metal interface, *i.e.*, Reaction [3]; and
(5) mass transfer of carbon in the metal in the case of a metal/slag reaction.

Numerous studies have been carried out on the kinetics of reduction of iron oxide from liquid slag by solid carbon or carbon dissolved in liquid metal. Nevertheless, there were large discrepancies among the results of different researchers regarding the magnitude of the rate and the controlling steps of the overall reaction. For a better understanding of the kinetics of the overall Reaction [1], sound knowledge about the rate of each individual step, from 1 through 5, is needed. Among these steps, the two interfacial chemical Reactions [2] and [3] are very important and could be the ultimate limit on how far we can go to enhance the bath-smelting process. The reaction of CO_2 with carbon in the liquid iron was the subject of several studies,[8–11] and consistent results were obtained. The reaction of CO_2 with solid carbon in the forms of char, graphite, and coke was also extensively studied, and, more recently, a comprehensive study[12] was carried out at temperatures and gas compositions pertinent to bath smelting. The knowledge of the rate of the carbon gasification reaction allowed one to re-evaluate its role in the complex system.[13] However, our knowledge of the rate phenomena for the gas/slag interfacial reaction, particularly for slag compositions pertinent to bath smelting, is by far inadequate.

The present study on the rates of the reduction of iron oxide in liquid slags by CO was undertaken to establish the magnitude of the rates and their dependence on the iron oxide content, basicity of the melt, and temperature. Based on the results, the possible role of this interfacial reaction in the overall reduction process was analyzed.

Y. LI, Senior Research Engineer, is with the Research and Technology Center, United State Steel, Monroeville, PA 15146. Contact e-mail: yli@uss.com I.P. RATCHEV, Principal Research Scientist, is with BHP Billiton Innovation, Newcastle Laboratories, Wallsend NSW 2287, Australia.

Manuscript submitted August 21, 2001.

II. EXPERIMENTAL DETAILS

A. *Apparatus and Materials*

The experimental setup is the same as the one used in a previous study.[14] A molybdenum-wound resistance furnace was equipped with a 52-mm-i.d. alumina working tube. The temperature was controlled by an EUROTHERM (Eurotherm Controls Inc., Worthing, West Sussex, UK) controller with a Pt-6 pct Rh/Pt-30 pct Rh (type B) thermocouple located close to the sample. The temperature profiles in the working tube were carefully measured under the same experimental conditions (such as the mass of the sample and the gas-flow condition) as those used in the kinetic experiments. A 50-mm-long hot zone was obtained, in which the temperature varied within ± 1.0 K. The liquid slag was contained in a platinum crucible, 25 mm in height and tapered from a 25-mm i.d. at the top to a 12-mm i.d. at the base. An alumina crucible, containing the platinum crucible and the slag, was attached to the balance through a platinum wire. The electrobalance (connected to a personal computer for data logging) was accurate to ± 0.1 mg. The gas delivery tube was a high-purity transparent silica tube of 10-mm o.d. and 8-mm i.d. The outlet of the gas delivery tube was located 5 to 10 mm above the surface of the melt.

The gases used in the experiments included CO (99.97 vol pct), CO_2 (99.9 vol pct), and Ar (99.99 vol pct), supplied by Linde Gas (Sydney). All the gases were passed through DRIERITE (Drierite Co., Xenia, OH) ($CaSO_4$) to remove moisture, and, except for CO_2, through Ascarite (granulated sodium hydroxide on a support) to remove CO_2. The Argon was further purified by passing through a bed of copper turnings at 873 K and magnesium turnings at 723 K to remove trace amounts of oxygen. The gas flow rates were controlled by a set of mass-flow controllers calibrated by means of soap-film burettes. Analytical-grade Fe_2O_3, $CaCO_3$, MgO, Al_2O_3, and SiO_2 were used to prepare the slags.

B. *Procedure*

To prepare the iron-free "master" slags, the mixtures of appropriate composition were melted in a 220 mL platinium crucible in air at 1873 K and quenched on a copper plate. The slags were then ground and remelted, followed by quenching and grinding. To prepare the sample for an experiment, 10 g of slag sample, including an appropriate amount of iron oxide in the form of Fe_2O_3, were put in a platinum crucible and melted in air at 1873 K. The slag was then quenched with the crucible.

In a typical experiment, the crucible, containing the slag sample, was introduced into the molybdenum furnace and attached to the balance. Under the flow of a gas mixture of known composition, the sample was heated to the required temperature. The sample was equilibrated with the gas before the commencement of the reduction. At the beginning of the reduction, the gas was changed to a CO-Ar mixture.

III. RESULTS

In the present study, the sample weight change, due to the removal of oxygen from the melts as a result of gas/slag interfacial reactions, was continuously measured. The reaction rate (v), in units of mol-O cm^{-2} s^{-1}, is given by

$$v = \frac{1}{16A}\frac{dw}{dt} \qquad [4]$$

where A is the surface area (cm^2) of the melt and dw/dt is the weight loss/gain rate (g/s). Based on the results of the cold model experiments,[15] the cross-sectional area of the crucible was taken as the surface area. The term dw/dt was evaluated from the continuously recorded sample weight.

The effects of mass transfer in the gas and liquid phases were eliminated experimentally in the same way as in a previous study.[14] The apparent first-order rate constant (k_a) was calculated from the measured rate using the equation

$$v = k_a\left(P_{CO} - P_{CO_2}\left(\frac{P_{CO_2}}{P_{CO}}\right)^{-1}_{eq.}\right) \qquad [5]$$

The initial slag compositions, including the Fe^{3+}/Fe^{2+} ratio, were obtained from the chemical analysis of the quenched slag samples from an independent experiment in which the same procedures were followed except for the reduction step. The change of the slag composition, primarily the change of the Fe^{3+}/Fe^{2+} ratio, during the reduction was calculated using the initial slag compositions and weight loss based on the mass-conservation law. Good agreement was found among the calculated and the analyzed compositions of the "end-point" slag. Weight-loss rates were obtained from linear regressions of weight *vs* time data over a short period of time, during which a fairly straight line was observed. The rates were assigned to the corresponding slag compositions. The effect of the oxidation state of the slags, iron oxide content, basicity, and temperature on the reduction rate of iron oxide were studied.

A. *The Effect of Iron Oxide Content in the Slags*

Three series of experiments were conducted using a master slag with a CaO/SiO_2 (wt pct) ratio of unity and an Al_2O_3 content of 15 to 20 wt pct.

In the first series of experiments, 5 to 90 wt pct of 'FeO' as Fe_2O_3 were added to the master slag 42.5CaO-42.5SiO_2-15Al_2O_3 (wt pct) and premelted in air in platinum crucibles. The slags, contained in the platinum crucible, were then put into the furnace and heated to 1773 K in argon. Weight loss due to the oxygen evolution, which accelerated after the slag was melted, was observed. The slag was kept at 1773 K under argon flow for 2 hours, until the rate of weight loss became negligible compared with that in the reduction stage. At that point, the gas was changed from argon to an Ar-CO mixture and the reduction commenced. Figures 1 and 2 show the effect of the iron oxide content and the oxidation state of the slag (represented as the Fe^{3+}/Fe^{2+} ratio) on the reduction-rate constant. The Fe^{3+}/Fe^{2+} ratios shown in Figures 1 and 2 were calculated from the Fe^{3+}/Fe^{2+} ratio at the beginning of the reduction and the weight loss. The rate increased with the increase of iron oxide content in the slags above ~20 wt pct 'FeO'. It remained essentially constant below 20 wt pct 'FeO'. This trend is clearly shown in Figure 3, in which the rates on different slags at an Fe^{3+}/Fe^{2+} ratio of 0.2 are plotted against the iron oxide content. Another feature of Figures 1 and 2 is that they show the reduction-rate decreases with the Fe^{3+}/Fe^{2+} ratio or, in other words, the oxygen potential of the slags. However, this dependence is rather weak when compared with that of oxidation of the

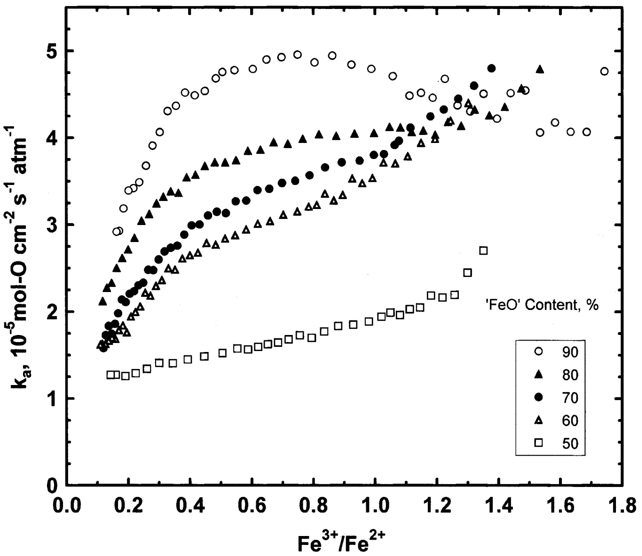


Fig. 1—The dependence of the reduction rate constant on the Fe^{3+}/Fe^{2+} ratio and iron oxide content for slags based on 42.5CaO-42.5 SiO_2-15Al_2O_3 (wt pct) containing 50 to 90 wt pct 'FeO' at 1773 K.

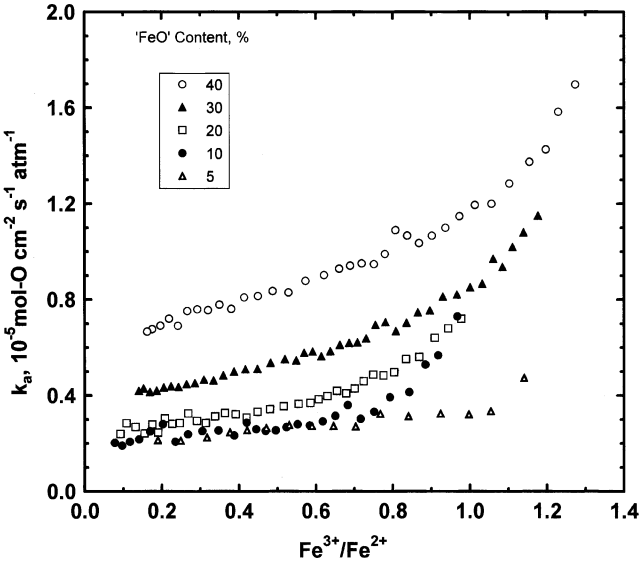


Fig. 2—The dependence of the reduction rate constant on the Fe^{3+}/Fe^{2+} ratio and iron oxide content for slags based on 42.5CaO-42.5 SiO_2-15Al_2O_3 (wt pct) containing 5 to 40 wt pct 'FeO' at 1773 K.

melt by CO_2. If the form $k_a = k_a' \, (Fe^{3+}/Fe^{2+})^{\alpha}$ is assumed, the exponent α will be 0.3 to 0.4 for the reduction, while the value for the oxidation was deduced to be -2 by Belton.[16] The rate data for slags with an iron oxide content of 80 wt pct or higher are likely to refer to two-phase systems at high values of the Fe^{3+}/Fe^{2+} ratio. Magnetite separation would occur if the Fe^{3+}/Fe^{2+} ratio exceeds about 0.73 with pure liquid iron oxide at 1773 K.[17] No direct data are available for the pertinent melts of the present study, but for aluminum-free calcium silicates containing 90 wt pct iron oxide, the data of Timucin and Morris[18] indicate that magnetite would separate at $Fe^{3+}/Fe^{2+} \approx 1$ at 1723 K.

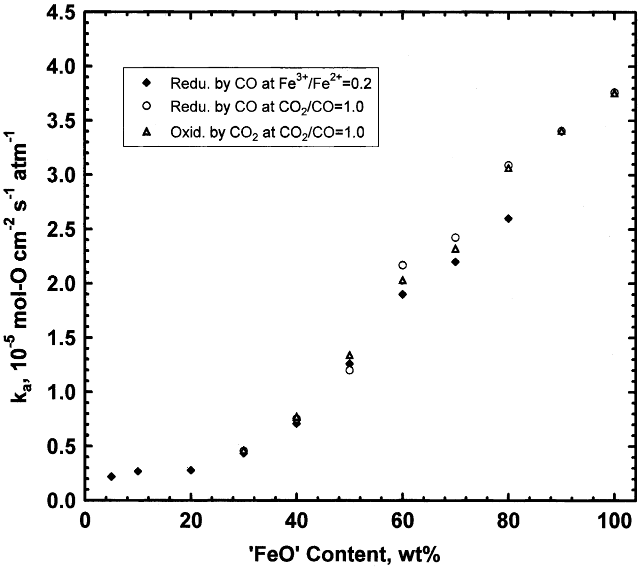


Fig. 3—The dependence of the apparent rate constant on iron oxide content in slags based on 42.5CaO-42.5SiO_2-15Al_2O_3 (wt pct) in equilibrium with a gas mixture with a CO_2/CO ratio of unity at 1773 K. Data represented by solid diamonds are taken from Figs. 1 and 2 at $Fe^{3+}/Fe^{2+} = 0.2$.

In the second series of experiments, the reduction and oxidation rates of iron oxide in slags, based on a 42.5CaO-42.5SiO_2-15Al_2O_3 (wt pct) slag containing 30 to 100 wt pct 'FeO' and pre-equilibrated with a gas mixture with a CO_2/CO ratio of unity, were measured. Figure 3 shows the results. Following the principle of microscopic reversibility, the oxidation rate by CO_2 and reduction rate by CO of the melts should be of equal value when the melt is pre-equilibrated at the oxygen potential of a CO_2/CO ratio of unity. The results shown in Figure 3 agree fairly well with this theoretical prediction. This is consistent with the equilibrium being indeed reached before the reduction- or oxidation-rate measurement commenced and, second, with the measured rates being those for the interfacial chemical reaction.

The Fe^{3+}/Fe^{2+} ratios in the melts with different iron oxide contents in equilibrium with a gas mixture having a CO_2/CO ratio of unity were measured, and the results are shown in Figure 4. The Fe^{3+}/Fe^{2+} ratio remained fairly constant, while the iron oxide content in the slags varied from 30 to 100 wt pct. A similar dependence of the equilibrium Fe^{3+}/Fe^{2+} ratio on iron oxide content at given CO_2/CO ratios was also found by Yang and Belton,[19] who studied the redox equilibria for a similar slag system containing 3 to 13 wt pct of iron oxide.

Taking data from Figures 1 and 2 at a fixed Fe^{3+}/Fe^{2+} ratio of 0.2, which is the value of the equilibrium Fe^{3+}/Fe^{2+} ratio at a CO_2/CO ratio of unity, the reduction-rate constants, obtained from the first series of experiments, are also plotted in Figure 3. The results from these two series of independent experiments agree very well.

In the third series of experiments, the reduction rate of iron oxide in slags, based on 40CaO-40SiO_2-20Al_2O_3 (wt pct) with varying Fe_xO contents and saturated with metallic iron, was measured at 1673 K. High-purity iron bars, made by melting electrolytic iron in a vacuum furnace, were used to make the iron crucibles with an i.d. of 24 mm and a height of 10 mm. Fe_xO was prepared by heating a mixture of equimolar pure iron powder and analytical-grade ferric oxide powder in an iron crucible at 1473 K in argon for 4 hours, followed by grinding and magnetic separation. The

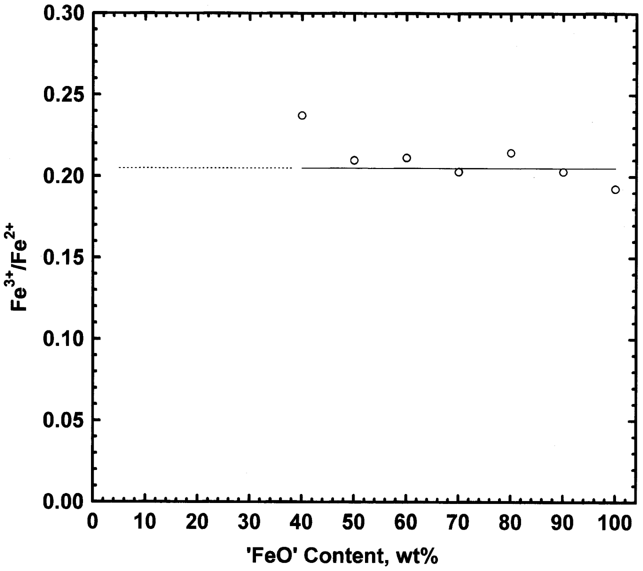


Fig. 4—Variation of the Fe^{3+}/Fe^{2+} ratio with iron oxide content in slags based on $42.5CaO-42.5SiO_2-15Al_2O_3$ (wt pct) in equilibrium with a gas mixture with a CO_2/CO ratio of unity at 1773 K.

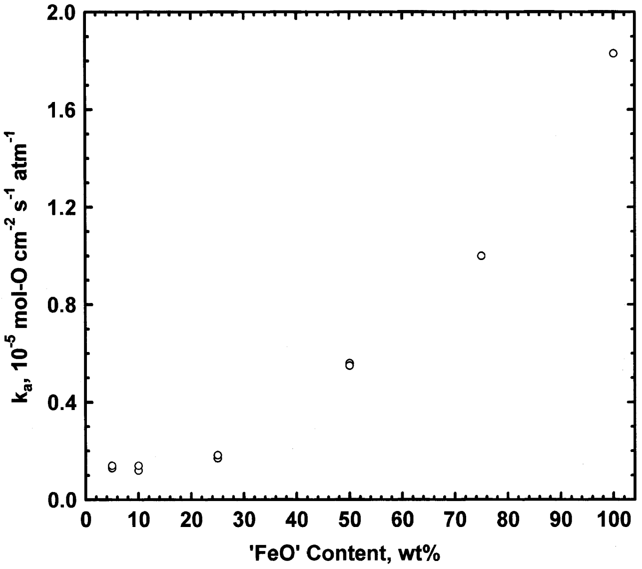


Fig. 5—Dependence of the reduction rate constant of iron oxide on 'FeO' content in iron-saturated $40CaO-40SiO_2-20Al_2O_3$ (wt pct) slag at 1673 K.

mixture of prefused master slags and the appropriate amount of wüstite was put into the iron crucible and heated to 1673 K in the furnace under the flow of ultrahigh-purity argon. The sample was kept at 1673 K for 2 hours to let the slag equilibrate with the metallic iron crucible before the reduction was conducted. Figure 5 shows the results of this series of experiments. The reduction rate decreased sharply with the decrease of the iron oxide content in the slag in the high-iron-oxide range from pure iron oxide to about 30 wt pct Fe_xO. The rate was essentially independent of iron oxide in the low-iron-oxide range, at least in the range from 5 to 20 wt pct Fe_xO.

B. *The Effect of Slag Basicity*

The effect of slag basicity on the reduction rate of iron oxide was studied in the $CaO-SiO_2-Al_2O_3-Fe_xO$ system.

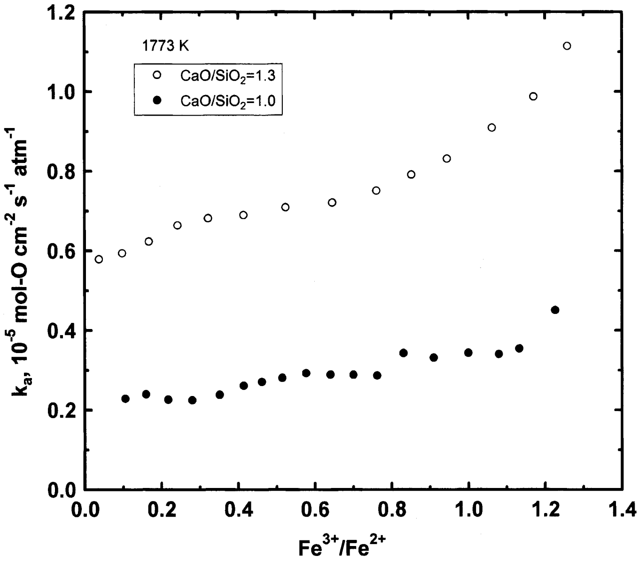


Fig. 6—Variation of the apparent rate constant for the reduction by CO at 1773 K of iron oxide with Fe^{3+}/Fe^{2+} ratio and slag basicity for slag $CaO-SiO_2-15Al_2O_3$ + 5 wt pct 'FeO'

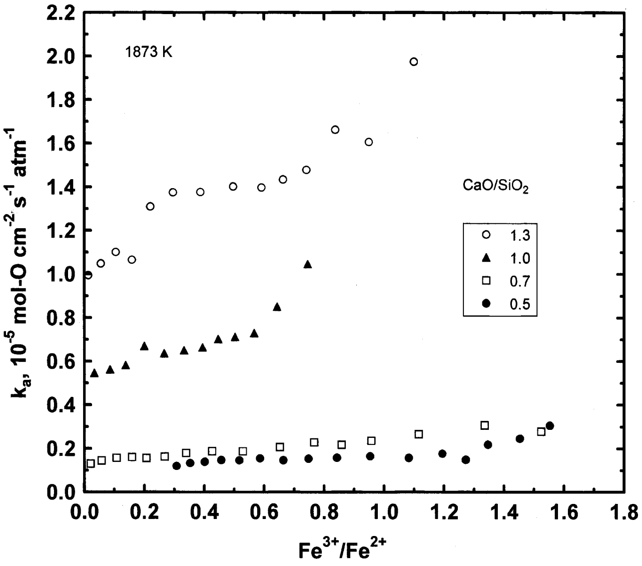


Fig. 7—Variation of the apparent rate constant for the reduction by CO of iron oxide with Fe^{3+}/Fe^{2+} ratio and slag basicity for slag $CaO-SiO_2-15Al_2O_3$ + 5 wt pct 'FeO' at 1873 K.

The 'FeO' and Al_2O_3 contents in the slags were kept at 5 and 15 wt pct, respectively. The CaO/SiO_2 ratio was varied from 1.0 to 1.3 at 1773 K and from 0.5 to 1.3 at 1873 K. The slag, contained in a platinum crucible and premelted in air at 1873 K, was heated and then kept at the experimental temperature for at least 2 hours until the rate of weight loss became negligible compared with that during reduction. An independent experiment was carried out to obtain the initial Fe^{3+}/Fe^{2+} ratio for each slag.

The effects of slag basicity on the reduction rate are shown in Figures 6 and 7. The reduction rate of iron oxide increased significantly with the increase in slag basicity. At 1773 K, the reduction rate of iron oxide in $CaO-SiO_2-15Al_2O_3-5Fe_xO$ was tripled when the CaO/SiO_2 ratio was increased from

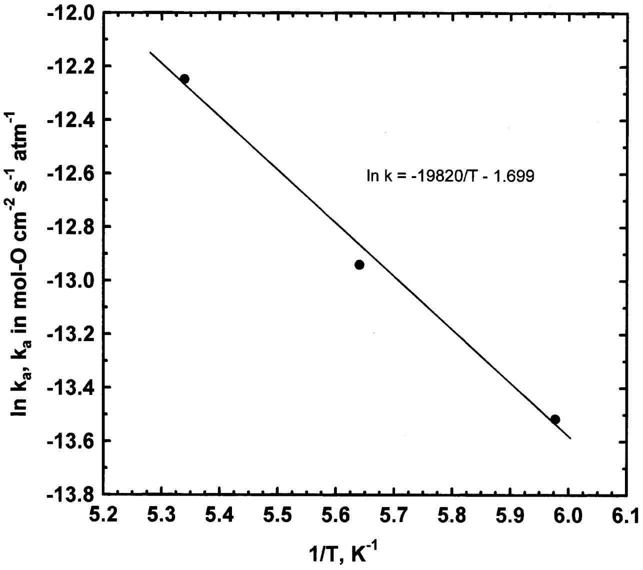


Fig. 8—Arrhenius plot of the apparent rate constant k for the reduction of iron oxide from 42.5CaO-42.5SiO$_2$-15Al$_2$O$_3$ + 5 wt pct 'FeO' slag to metallic iron.

1.0 to 1.3, as shown in Figure 6. Similar trends were observed at 1873 K for a wider range of CaO/SiO$_2$ ratios, as shown in Figure 7. The activity of FeO, of course, will increase with the increase of slag basicity. The activities of iron oxide in a CaO-SiO$_2$-Al$_2$O$_3$-5 wt pct 'FeO' slag system with a CaO/SiO$_2$ ratio of 1.0 and 1.3 are calculated to be 0.0788 and 0.0979, respectively. The difference of the iron oxide activities in these two slags was only 24 pct and, therefore, cannot explain the large difference in the rate.

C. *The Effect of Temperature*

The effect of temperature on the reduction rate of iron oxide in a CaO-SiO$_2$-Al$_2$O$_3$ + 5 wt pct 'FeO' slag with a CaO/SiO$_2$ ratio of 1.0 is shown in Figure 8. The data at 1673 K are taken from the experimental results for the reduction of iron oxide in iron-saturated 40CaO-40SiO$_2$-20Al$_2$O$_3$ + 5 wt pct 'FeO'. The data at 1773 and 1873 K are taken from the experimental results for continuous reduction of iron oxide in the 42.5CaO-42.5SiO$_2$-15Al$_2$O$_3$ + 5 wt pct 'FeO' slag, as shown in Figures 6 and 7, where the Fe^{3+}/Fe^{2+} ratio is approximately the same as the one in equilibrium with metallic iron. The Arrhenius plot of these data, as shown in Figure 8, gives

$$\ln k_a = -19{,}820/T - 1.699 \qquad [6]$$

The activation energy, calculated from the equation, is 165 kJ/mol.

IV. DISCUSSION

A. *The Effect of Iron Oxide Content on the Reduction Rate*

For the reduction of iron oxide in slags by CO, we may tend to write the reaction equation as Eq. [2] and assume that the reaction rate is proportional to the activities of the reactants, *i.e*,

$$v = k a_{FeO} P_{\mathrm{CO}} \left(1 - \frac{1}{K_2} \frac{a_{\mathrm{Fe}} P_{\mathrm{CO_2}}}{a_{\mathrm{FeO}} P_{\mathrm{CO}}}\right) \qquad [7]$$

where the term in the parentheses denotes the departure from equilibrium, and k is expected to be a function of temperature only. If the amount of CO$_2$ in the gas phase is negligible, as in the case in which high-purity CO and Ar mixtures are used as a reductant and the partial pressure of produced CO$_2$ is negligibly small, the term in the parentheses of Eq. [7] becomes 1.0. The apparent first-order (with respect to P_{CO}) rate constant (k_a) would then be proportional to the activity of iron oxide. Experimental results show that this is not the case. Nagasaka *et al.*[20] found that the addition of a basic oxide to pure iron oxide, which will definitely decrease the activity of FeO, actually *increases* the reduction rate. Results of the present authors[15] on the reduction rates for binary systems support Nagasaka's conclusion. This phenomenon cannot be explained by Eq. [7], even if we put an exponent of positive value other than 1.0 to a_{FeO}. However, one might attribute the higher reduction rate to the higher Fe^{3+}/Fe^{2+} ratio in the basic melts than that in pure iron oxide, by assuming that Fe^{3+} can be reduced by CO "more easily" than Fe^{2+}. If this assumption is valid, following the same logic, we would expect *lower* oxidation rates on basic melts, like CaO-Fe$_x$O, than on pure iron oxides. However, experimental results[21] showed that, at a given oxygen potential, the oxidation rates on Fe$_x$O-CaO melts are *higher* than those on pure iron oxide, despite the higher Fe^{3+}/Fe^{2+} ratios. Details about the effect of slag basicity on the reaction rate will be discussed in the next section.

The previous discussion indicates that no simple rate law, like Eq. [7], can be used to describe the effect of iron oxide content on the reaction rate. It also warns us that caution must be taken when we try to deduce a rate law from a stoichiometric chemical-reaction equation. The reaction must be *elementary* and represent the *true rate-controlling step* if such attempt is to be made. Reaction [2] is an overall reaction in which several elementary reactions, *e.g.*, adsorption, combination, and desorption, are involved. Details of the reaction mechanisms can be found elsewhere.[14,16]

For the aforementioned reason, no attempt is made to deduce a rate law concerning the iron oxide content in slags. General trends are discussed qualitatively, and appropriate comparisons to other studies are made quantitatively.

Figure 9 shows the dependence of the apparent rate constants on iron oxide contents for slags based on 40CaO-40SiO$_2$-20Al$_2$O$_3$ saturated with metallic iron at 1673 K (solid circles) and for 42.5CaO-42.5SiO$_2$-15Al$_2$O$_3$ at an Fe^{3+}/Fe^{2+} ratio of 0.2 and at 1773 K (solid triangles). Similar trends can be seen at both temperatures. The rates at 1773 K are approximately twice as high as those at 1673 K at the same iron oxide content in the slags. In the low-iron range (5 to 20 wt pct 'FeO'), the reduction rate is essentially constant. In the middle-iron range (20 to 60 wt pct 'FeO'), the reduction rate increases sharply with the increase of the iron oxide content. In iron-rich slags (60 to 100 wt pct 'FeO'), the reduction rate increases, at a lower rate, with the increase of the iron content. It should be noted that the rate in the very-low-iron range ($<$5 wt pct FeO) was not measured. In that range, very low CO partial pressures ($<$0.01 atm) must be used in order to overcome the liquid-phase diffusion limitation. Problems associated with this range include difficulty in preparing the gas mixture precisely and the slow

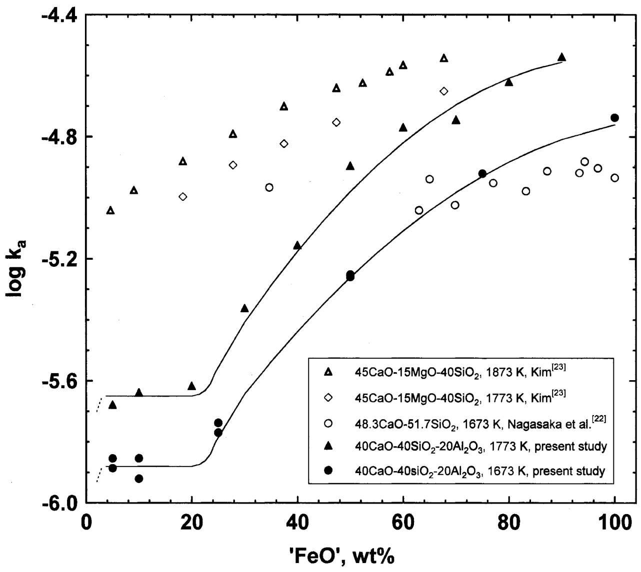


Fig. 9—Dependence of the apparent rate constant for the reduction of iron oxide by CO on iron oxide content in slags.

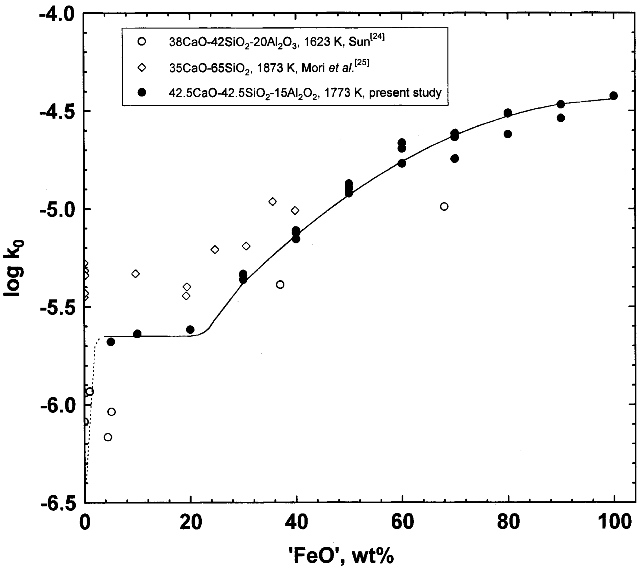


Fig. 10—Dependence of the apparent rate constant on iron oxide content in slag equilibrium with CO_2/CO ratio of 1.0.

rate, which precludes accurate measurement with the present setup. However, the results of the "blank" experiments on "pure" master slags (slags without iron oxide) showed negligibly low rates. Accordingly, there may be a sharp drop somewhere below 5 wt pct 'FeO,' as depicted by the dotted lines in Figure 9.

Nagasaka *et al.*[22] studied the reduction rate of iron oxide in a master slag with equal CaO and SiO_2 molar contents, contained in metallic iron crucibles at 1673 K. Their results, as shown by the open circles in Figure 9, show a very slight change as the iron oxide content varied between 35 and 100 wt pct. The results from the present study, under similar conditions, disagree with their results. Kim[23] studied the dependence of the reduction rates on the iron oxide contents in a master slag of 45CaO-15MgO-40SiO$_2$. Initially, the slags were in equilibrium with gas mixtures, having a CO_2/CO ratio of 0.2. His results are also shown in Figure 9 as triangles and diamonds at 1873 and 1773 K, respectively. By comparing the two sets of data at 1773 K, it is seen that at high iron oxide contents, Kim's results tend to agree with the results from the present study, while at low iron oxide contents, Kim's values are much higher. For example, at 20 wt pct 'FeO', his value is 4 times that of the present study. This may largely be due to the higher basicity of his slag. The (CaO + MgO)/SiO_2 ratio of his master slag is 1.5, while the one used in the present study is 1.0. As shown in Figure 6, the reduction rate of iron oxide is tripled when the CaO/SiO_2 ratio is raised from 1.0 to 1.3. The effect of master-slag basicity on the rate is expected to decrease with the increase of iron oxide content and, ultimately, disappear when the iron oxide content approaches 100 wt pct. Experimental results show agreement with this consideration. Another reason for Kim's higher rate may be the larger uncertainty in his measurement when the iron content becomes lower, due to the generation of CO_2 from the carbon deposition reaction. For example, the measured CO_2 concentration in the off gas of a blank experiment was 173.3 ppm when a 1 vol pct CO-Ar mixture was used. This translates to a rate constant of 8.79×10^{-6} mol-O cm^{-2} s^{-1} atm^{-1}, which is about 90 pct of the value of the rate constant he claimed for a 20 pct FeO slag at 1773 K.

The dependence of the apparent rate constant (k_0), for slags in equilibrium with a CO_2/CO ratio of 1.0, on iron oxide content is presented in Figure 10. In addition to the results from the present work, results from isotope-exchange studies performed by Sun[24] and Mori *et al.*[25] are presented for comparison. Similar trends, *i.e.*, a nearly constant rate in the low-iron range (<20 wt pct 'FeO') and a sharp increase in the middle-iron range, are followed by results from all three studies. Compared to the present study, Sun's results show lower rates, presumably due to the lower temperature. Mori's results, on the other hand, show slightly higher rates, while the temperature employed was higher.

In a previously published article,[14] the kinetics of the reaction between liquid iron oxide and CO-CO_2 gases was described by a "charge-transfer" model. Since charge transfer is involved in the reaction processes, the electrical conductivity of the melts is expected to affect the reaction rate. Figure 11 shows the variation of the electrical conductivity of CaO-SiO$_2$(-Al$_2$O$_3$)-FeO slags with the iron oxide content. The Data include results from studies by Narita *et al.*,[26] Kato and Minowa,[27] Adachi and Ogino,[28] and Fontana *et al.*[29] By comparing Figure 11 to Figures 3 and 5, a similarity can be seen between the dependence of the reaction rate and electrical conductivity on the iron oxide content in the melts. On the other hand, the a_{FeO}-'FeO' wt pct curve, as shown in Figure 12, differs significantly from the rate-'FeO' wt pct curves shown in Figures 3 and 5. This indicates, again, that the activity of iron oxide, a thermodynamic property of the bulk slag, plays, if any, a minor role in the gas/slag interfacial kinetics.

B. *The Effect of Slag Basicity on the Reaction Rate*

The effect of slag basicity on the rate of reduction of Fe$_x$O in slags by CO cannot be perceived directly, because its relevant components, *e.g.*, CaO, MgO, and SiO_2, do not directly take part in the reactions. However, some physical

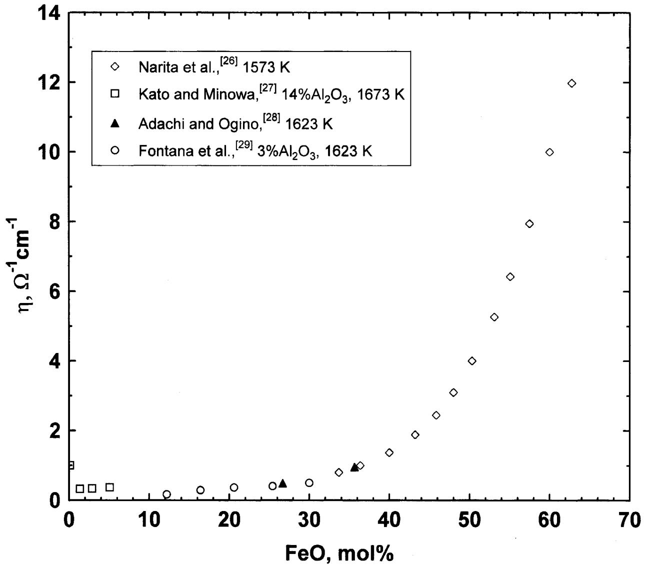


Fig. 11—The electrical conductivity of CaO-SiO$_2$ (Al$_2$O$_3$) melts with CaO/SiO$_2$ ratio of 1.0 as a function of 'FeO' content.

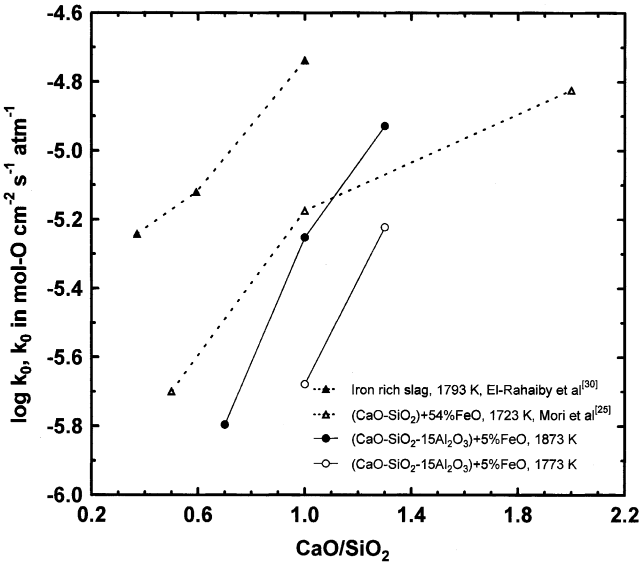


Fig. 13—The effect of slag basicity on reduction and oxidation rates of iron oxides by CO-CO$_2$ gases.

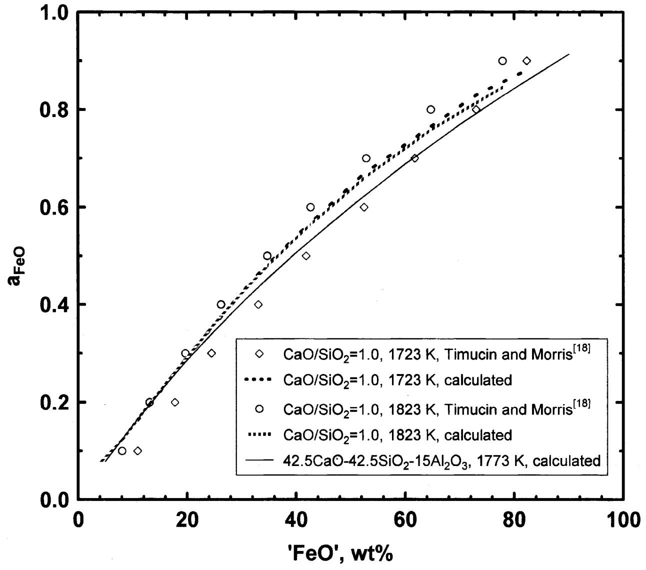


Fig. 12—The activity of iron oxide in CaO-SiO$_2$ (-Al$_2$O$_3$) melts with varying amounts of 'FeO'. Lines represent the calculated values using the KFS model developed by CSIRO (Melbourne, Victoria, Australia).

or thermodynamic properties that may be relevant to the reaction rate, such as the surface tension, electrical conductivity, redox equilibria, and activity of FeO, are affected by the slag basicity.

Figure 13 shows the effect of slag basicity on the reduction and oxidation rate of iron oxide by CO-CO$_2$ gases. It can be seen that the reduction rate of iron oxide increases sharply with the increase of slag basicity. For example, at 1773 K, the reduction rate of iron oxide (5 wt pct) is tripled when the CaO/SiO$_2$ ratio increases from 1.0 to 1.3 Also shown in Figure 13 are results of the CO$_2$ dissociation rates on calcium iron silicates, measured by El-Rahaiby *et al.*[30] and Mori *et al.*[25] using the isotope-exchange technique. These rates can be regarded as the oxidation rates of iron oxide by CO$_2$. A trend similar to that of reduction was observed. This trend was also observed by Nagasaka *et al.*,[22] Tran,[31] and Kim[23] when they studied the reduction rate of iron oxide in CaO-MgO-SiO$_2$ slags and by Jahanshahi and Wright[32] when they studied the reduction of lead slags. It is now generally accepted that the increase of basicity will increase the rates. However, the reason(s) for this kind of dependence are still under debate. Several opinions are presented and discussed below.

1. *The reaction rate increases with the increase of slag basicity because of the increase of the iron oxide activity coefficient*

In the CaO-SiO$_2$(-Al$_2$O$_3$) slag, the activity coefficient of iron oxide was found to increase with the increase of basicity when CaO/SiO$_2$ < 2.0.[18,33,35] For low-iron slags, Timucin and Morris's results[18] showed a very weak dependence. Taniguchi, Morita, and Sano's results[33] showed a relatively stronger dependence. Even taking the latter results, the activity of iron oxide is expected to increase by only 30 pct when the CaO/SiO$_2$ ratio increases from 1.0 to 1.5. If this factor were used to normalize the 'FeO' contents of the slags containing 5 wt pct 'FeO' but having different CaO/SiO$_2$ ratios, they would all fall into the range (FeO $<$ 20 wt pct) where the reaction rate was found to be essentially constant, as discussed in the previous section. Furthermore, the CO$_2$ dissociation rate was found to increase with the increase of the CaO/SiO$_2$ ratio all the way up to 11.0, where γ_{FeO} certainly will decrease.[30] Therefore, the change of iron oxide activity cannot be used to explain the effect of slag basicity on the gas/slag interfacial reaction rate.

2. *With the increase of slag basicity, the Fe^{3+}/Fe^{2+} ratio in the slag increases and, since Fe^{3+} (Fe_2O_3) is more easily reduced than Fe^{2+} (FeO), the reduction rate increases.*

At a given oxygen potential, the Fe^{3+}/Fe^{2+} ratio in the slag increases with the increase of slag basicity. Thermodynamically, Fe^{3+} (or Fe_2O_3) is more easily reduced than Fe^{2+} (or FeO). However, this fact does not necessarily mean that the reduction *rate*, a kinetic quantity, of Fe^{3+} is higher than that of Fe^{2+}. Even if it does, as it may, we can only rationalize that the reduction rate will increase with the increase of basicity. Based on the same logic, we will expect that the oxidation rate of iron oxides should *decrease* with the increase of slag basicity. The experimental results from isotope-exchange studies, as shown in Figure 13, show the opposite. Therefore, this statement may be rejected.

3. Tran[31] and Jahanshashi and Wright[32] explained the effect of basicity on reaction rate in terms of the activity of free oxygen ($a_{O^{2-}}$) and/or the Fe^{3+}/Fe^{2+} ratio at the gas/slag interface according to the following steps involved in the formation of CO_2 species:

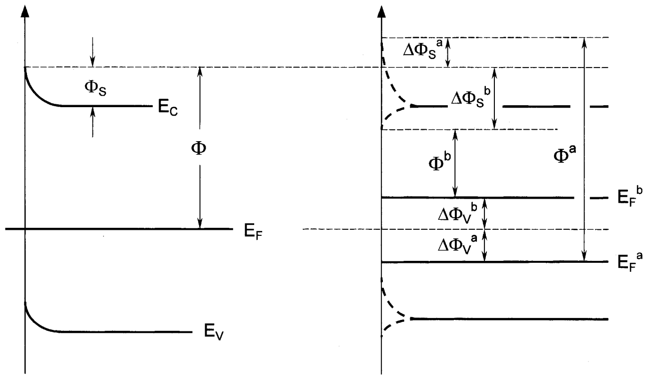
$$CO_{(g)} + (O^{2-})_{slag} = CO_{2(ads)}{}^{2-} \qquad [8]$$

$$CO_{2(ads)}{}^{2-} + 2(Fe^{3+}) = 2(Fe^{2+}) + CO_{2(g)} \qquad [9]$$

An increase in slag basicity will increase the activity of the oxygen ion and the Fe^{3+}/Fe^{2+} ratio. Accordingly, the driving forces of Reactions [8] and [9] will increase and, hence, the reaction rate will increase. Similar to the arguments in statement 2, this opinion can be rejected by considering the oxidation rate of the melts.

4. *Occupation of reaction sites by surface-active components such as* SiO_2

In case of the gas-metal reaction, the "surface-blockage" model, considering the occupation of reaction sites by surface-active elements such as O, S, Se, *etc.*, was successfully used to explain the rate phenomena.[16] There is good reason to consider the surface constitution of the slag when we deal with the gas/slag interfacial reaction rate. In fact, Fine *et al.*,[36] acknowledging this effect, used the expression $k(1 - 0.7(a_{SiO_2})^{1/3})\,(a_{FeO}P_{CO} - a_{Fe}P_{CO_2})$, where the first term in parentheses reflects the reduction of surface sites by silica, to explain their experimental results. Richardson[37] has analyzed the available surface-tension data for liquid binary iron silicates at 1420 °C and has shown that at bulk saturation with solid silica, the surface is still unsaturated. The surface coverage by SiO_2 was deduced to be about 70 pct. The observed apparent rate constant at 1500 °C and $CO_2/CO = 1.0$ decreases from 4.1 to 1.0×10^{-5} mol-O cm^{-2} s^{-1} when 30 wt pct silica was added to liquid iron oxide. This is a somewhat larger decrease than the expectation from the consideration of surface constitution. A recent publication by Sun and Belton[38] showed that the effects of two strong surfactants, P_2O_5 and Na_2O, on the gas (CO-CO_2)/slag (liquid iron oxide) interfacial reaction rates are totally opposite: while the addition of P_2O_5 significantly decreases the rate, which is in accordance with the surface-blockage consideration, the addition of Na_2O significantly *increases* the rate. The failure of using the surface-blockage model to explain the gas/slag interfacial-rate phenomena may be due to the fact that the surface (even the bulk) constitution of slags is far more complex than that of metal. Liquid metal can be treated as a homogeneous mixture of atoms in the bulk and concentrated surfactant atoms on the surface. The surface-segregation phenomena of metal, at least in the solid state at elevated temperatures, have been studied directly.[39,40] The availability of a large amount of data on surface tension (an indirect form of information on adsorption equilibria for liquid alloys) allows reasonably good estimates of the surface coverage. A liquid slag, on the other hand, is a mixture of different cations and anions. The nature of these ions and, hence, the structure of the slags, changes with slag compositions and is not yet fully understood. Mills and Keene[41] have reviewed the available surface-tension data for slags containing iron oxide. Broadly, the surface tensions of pure liquid oxides and slags are lower than for the metals, and the magnitude of the depression of the surface tension by surface-active components tends to be very much lower than, for example, that by the Group VI elements in liquid iron. It may be, for this reason, that the surface-constitution change plays only a minor role on the gas/slag interfacial reaction-rate phenomena.



(*a*) (*b*)

Fig. 14—Simplified energy band diagram assumed for liquid 'FeO': (*a*) pure iron oxide or CaO-SiO_2-Al_2O_3-'FeO' with $CaO/SiO_2 = 1.0$ and (*b*) the addition of basic oxides (superscript b) or acidic oxide (superscript a).

5. *Charge-transfer consideration*

Molten slag is a mixture of different ions. Transition metals, like iron and titanium, regardless of their exact forms, exist in slags as ions. The reduction or oxidation of iron and titanium in slag from one valence to another inevitably involves the transfer of charge. This means, for the gaseous species CO and CO_2, in the course of changing from one to another, there must be intermediate, adsorptive, *charged* radicals on the surface of the slag. For a given coverage of the surface and partial pressures in the gas phase, the number of active forms of such radicals, hence, the reaction rate, depends on the position of the Fermi level: the electrochemical potential of the electrons.[42]

The energy change for the transfer of electrons to reactants is given by the difference between the energy of the electrons in the bottom of the conduction band at the surface and the Fermi energy.

This is represented by the simplified energy-band diagram in Figure 14(a). In this Figure, the bottom of the conduction band in the bulk of the melt is represented by the level E_C, and the top of the valence band in the bulk is represented by the level E_V. In general, a space charge will exist due to excess negative or positive ions at the surface. This results in bending of the conduction and valence bands upward in case of excess negative ions at the surface, or downward in case of excess positive ions at the surface. The change in the energy by the surface potential (Φ_S) is shown to be toward higher electron energy, on the assumption that surface "lattice" O^{2-} ions have less than the normal complement of cations. This assumption is not important to the discussion. The Fermi energy is indicated by the level E_F, and the difference in energy between electrons at the bottom of the

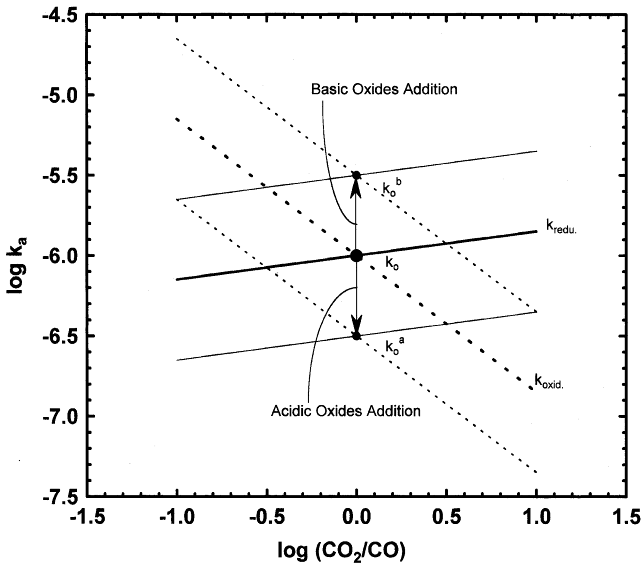


Fig. 15—Schematic diagram of the apparent rate constants showing the effect of slag basicity on the reduction and oxidation rates.

conduction band at the surface and the Fermi energy is indicated by $\Phi = E_C + \Phi_S - E_F$. For an "acceptor" reaction, such as

$$CO_{2(ad)} + 2e^- \rightarrow O^{2-}{}_{(ad)} + CO_{(ad)} \qquad [10]$$

the rate can be expressed as[38]

$$v = k' \, P_{CO_2} \exp \frac{-2\Phi}{\kappa T} \qquad [11]$$

where k' is a function of the temperature and density of surface reaction sites, and κ is the Boltzmann constant. Let's now assume that Figure 14(a) represents the case of pure liquid iron oxide or liquid CaO-SiO_2-Al_2O_3-FeO (CSAF) slags with a CaO/SiO_2 ratio of 1.0 in equilibrium with CO/CO_2 = 1.0. When "basic" oxides, such as CaO, are added to the pure liquid iron oxide or CSAF slags, both the bulk and the surface properties of the melts will change. For the bulk, the Fermi level will be displaced to a higher position, with a change of $\Delta\Phi_V{}^b$, because more-basic oxides have a higher Fermi energy.[43] For the surface, the conduction band and valence band will bend downward for $\Delta\Phi_S{}^b$, because of the segregation of 'CaO' leading to an increase in the cation (Ca^{2+}) concentration at the surface. The addition of an acidic oxide such as SiO_2 and P_2O_5 has the opposite effect, as shown in Figure 15(b). For such a potential change, Eq. [11] becomes

$$v^b = k' \, P_{CO_2} \exp \frac{-2\Phi^b}{\kappa T} \qquad [12a]$$

where Φ^b is the the difference in energy between electrons at the bottom of the conduction band at the surface and the Fermi energy for the melt with a basic oxides addition, and

$$v^a = k' \, P_{CO_2} \exp \frac{-2\Phi^a}{\kappa T} \qquad [12b]$$

where Φ^a is the difference in energy between electrons at the bottom of the conduction band at the surface and the Fermi energy for the melt with an acidic oxides addition. It can be easily found from Figure 15(b) that $\Phi^b = \Phi - \Delta\Phi_V{}^b - \Delta\Phi_S{}^b$ and $\Phi^a = \Phi + \Delta\Phi_V{}^a + \Delta\Phi_S{}^a$. For the relative rate or apparent rate-constant (note here that CO_2/CO = 1.0) change, it follows that

$$\ln \frac{v^b}{v} = \ln \frac{k_0^b}{k_0} = -\frac{2(\Phi^b - \Phi)}{\kappa T} = \frac{2(\Delta\Phi_s^b + \Delta\Phi_v^b)}{\kappa T} \qquad [13]$$

for the addition of basic oxides, and

$$\ln \frac{v^a}{v} = \ln \frac{k_0^a}{k_0} = -\frac{2(\Phi^a - \Phi)}{\kappa T} = -\frac{2(\Delta\Phi_s^a + \Delta\Phi_v^a)}{\kappa T} \qquad [14]$$

for the addition of acidic oxides.

Equations [13] and [14] clearly show that the addition of basic oxides will increase the apparent rate constant, and the addition of acidic oxides has the opposite effect. This is depicted in Figure 15, where k_0 represents the apparent rate constant for a melt (base case) equilibrated with a CO_2/CO ratio of 1.0, and k_0^b and k_0^a represent the change of k_0 with the addition of basic oxides and acidic oxides to the base melt, respectively. Following the microscopic reversibility of the reaction, the apparent rate constants for reduction and oxidation are identical at a CO_2/CO ratio of 1.0. It was found in this and previous studies[14] that with the increasing oxidation state of the slag, denoted by the CO_2/CO ratio in Figure 15, the apparent reduction-rate constant slightly increases and the apparent oxidation-rate constant sharply decreases. In Figure 15, the solid and dashed lines represent the apparent rate constants of reduction and oxidation, respectively. A detailed discussion on the relationship between the reduction- and oxidation-rate constants can be found in our previous publication.[14]

No experimental data are available for the change of the potential of the surface and bulk ($\Delta\Phi_S$ and $\Delta\Phi_V$) with the slag composition change. Thus, quantitative analysis is not possible at this stage. At 1773 K, one order of magnitude of rate change corresponds to a potential change of 0.18 eV. This value is not physically impossible, recognizing that the difference of the Fermi energy between CaO and SiO_2 is about 1.736 eV.[43]

V. CONCLUSIONS

The rates of interfacial reaction between molten CaO-SiO_2-Al_2O_3-Fe_xO and CO-CO_2 were measured using a gravimetric technique, where the mass-transfer rates in the gas phase and liquid slag were sufficiently high compared to the interfacial reaction rate. Based on the experimental results, the following conclusions can be made.

1. For slags of the CaO-SiO_2-Al_2O_3-Fe_xO system at a fixed oxidation state, the apparent rate constant decreased with 'FeO' content from 100 to 20 wt pct, whereas it remained essentially constant in the range from 5 to 20 wt pct. No direct relationship between the rate of the interfacial reaction and the activity of iron oxide could be established.

2. For $(40CaO\text{-}40SiO_2\text{-}20Al_2O_3) + Fe_xO$ slags in equilibrium with solid iron at 1673 K, the rate constants decreased from 1.84×10^{-5} mol-O cm^{-2} s^{-1} atm^{-1} for pure Fe_xO to 1.4×10^{-6} mol-O cm^{-2} s^{-1} atm^{-1} for slags containing 20 wt pct 'FeO.'
3. The reduction rate of iron oxide in slags of the $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_xO$ system increased significantly with an increase in the basicity.
4. The apparent reduction-rate constant of iron oxide in the $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_xO$ system depends relatively weakly on the oxidation state of the melts. In terms of $k = k'(Fe^{3+}/Fe^{2+})^{\alpha}$, the values of α range from 0.15 to 0.25.
5. The effect of temperatures in the range from 1400 °C to 1600 °C on the reduction rate of iron oxide from a $(42.5CaO\text{-}42.5SiO_2\text{-}15Al_2O_3) + 5$ wt pct FeO slag was studied. The calculated activation energy, based on these results, was 165 kJ/mol.

ACKNOWLEDGMENTS

This article is a tribute to Dr. G.R. Belton who was the supervisor of one of the author's (YL) Ph.D. thesis from which most of the work presented in this article was taken. The experimental work was carried out in the Newcastle Laboratory of BHP Research (Australia). Financial support by BHP Research for this project is appreciated.

REFERENCES

1. M.W. Davies, G.S.F. Hazeldean, and P.N. Smith: *Physical Chemistry of Process Metallurgy: the Richardson Conf.*, J.H.E. Jeffes and R.J. Tait, eds., The Institute of Mining and Metallurgy, London, 1973, pp. 95-107.
2. E.W. Mulholland, G.S.F. Hazeldean, and M.W. Davies: *J. Iron Steel Inst.*, 1973, vol. 211, pp. 632-39.
3. K. Ishii and Y. Kashiawaya: *3rd Int. Conf. on Molten Slags and Fluxes*, Glasgow, United Kingdom, The Institute of Metals, London, 1989, pp. 142-45.
4. Y. Ogawa and N. Tokumitsu: *Proc. 6th Int. Iron and Steel Congr.*, Nagoya, Japan, Iron and Steel Institute of Japan, Tokyo, 1990, pp. 147-52.
5. S. Hara and K. Ogino: *Tetsu-to-Hagané*, 1990, vol. 76, pp. 360-67.
6. D.J. Min and R.J. Fruehan: *Metall. Mater. Trans. B*, 1992, vol. 23B, pp. 29-37.
7. B. Sarma, A.W. Cramb, and R.J. Fruehan: *Metall. Mater. Trans. B*, 1996, vol. 27B, pp. 717-30.
8. D.R. Sain and G.R. Belton: *Metall. Mater. Trans. B*, 1976, vol. 7B, pp. 235-44.
9. D.R. Sain and G.R. Belton: *Metall. Mater. Trans. B*, 1978, vol. 9B, pp. 403-07.
10. F.J. Mannion and R.J. Fruehan: *Metall. Mater. Trans. B*, 1989, vol. 20B, pp. 853-61.
11. T. Nagasaka and R.J. Fruehan: *Metall. Mater. Trans. B*, 1994, vol. 25B, pp. 245-53.
12. S.R. Story and R.J. Fruehan: *Metall. Mater. Trans. B*, 2000, vol. 31B, pp. 43-54.
13. S.R. Story, B. Sarma, R.J. Fruehan, A.W. Cramb, and G.R. Belton: *Metall. Mater. Trans. B*, 1998, vol. 29B, pp. 935-38.
14. Y. Li, I.P. Ratchev, J.A. Lucas, G.M. Evans, and G.R. Belton: *Metall. Mater. Trans. B*, 2000, vol. 31B, pp. 1049-57.
15. Y. Li: Ph.D. Thesis, University of Newcastle, NSW, Australia, 1999.
16. G.R. Belton: *Advanced Physical Chemistry for Process Metallurgy*, Academic Press Ltd., New York, NY, 1997, pp. 183-218.
17. L.S. Darken and R.W. Gurry: *J. Am. Chem. Soc.*, 1946, vol. 68, pp. 798-816.
18. M. Timucin and A.E. Morris: *Metall. Trans.*, 1970, vol. 1, pp. 3193-201.
19. L. Yang and G.R. Belton: *Metall. Mater. Trans. B*, 1998, vol. 29B, pp. 837-45.
20. T. Nagasaka, Y. Iguchi, and S. Ban-ya: *5th Int. Iron and Steel Congr.: Process Technology Proc.*, ISS, Washington, DC, 1986, vol. 6, pp. 669-78.
21. Y. Sasaki, S. Hara, D.R. Gaskell, and G.R. Belton: *Metall. Mater. Trans. B*, 1984, vol. 15B, pp. 563-71.
22. T. Nagasaka, Y. Iguchi and S. Ban-Ya: *Tetsu-to-Hagané*, 1989, vol. 75, pp. 74-81.
23. W.M. Kim: Ph.D. Thesis, University of Kentucky, Lexington, KY, 1990.
24. S. Sun: Ph.D. Thesis, University of Newcastle, NSW, Australia, 1988.
25. M. Mori, K. Morita, and N. Sano: *Iron Steel Inst. Jpn. Int.*, 1996, vol. 36, pp. 624-30.
26. K. Narita, T. Onoye, T. Ishii, and K. Uemura: *Tetsu-to-Hagané*, 1975, vol. 61, pp. 2943-51.
27. M. Kato and S. Minowa: *Trans. Iron Steel Inst. Jpn.*, 1969, vol. 9, pp. 39-46.
28. A. Adachi and K. Ogino: *Yoyuen (Fused Salt)*, 1961, vol. 1, p. 151.
29. A. Fontana, L. Segeres, K. Twite, and R. Winand: *113th AIME Annual Meeting*, Los Angeles, CA, Feb. 1984, The Metallurgical Society of AIME, Warrendale, PA, 1984, TMS paper no. A 84-38.
30. S.K. El-Rahaiby, Y. Sasaki, D.R. Gaskell, and G.R. Belton: *Metall. Mater. Trans. B*, 1986, vol. 17B, pp. 307-16.
31. T. Tran: Ph.D. Thesis, University of Melbourne, Melbourne, Victoria, Australia, 1997.
32. S. Jahanshahi and S. Wright: *4th Int. Conf. on Molten Slags and Fluxes*, Sendai, Japan, Iron and Steel Institute of Japan, Tokyo, 1992, pp. 572-77.
33. Y. Taniguchi, K. Morita, and N. Sano: *Iron Steel Inst. Jpn. Int.*, 1997, vol. 37, pp. 956-61.
34. T. Ogura, R. Fujiwara, R. Mochizuki, Y. Kawamoto, T. Oishi, and M. Iwase: *Metall. Mater. Trans. B*, 1992, vol. 23B, pp. 456-66.
35. T. Arato, M. Tokuda, and M. Ohtani: *Tetsu-to-Hagané*, 1982, vol. 68, pp. 2263-70.
36. H.A. Fine, D. Meyer, D. Janke, and H.J. Engell: *Ironmaking and Steelmaking*, 1985, vol. 12, pp. 157-62.
37. F.D. Richardson: *Physical Chemistry of Melts in Metallurgy*, Academic Press Inc., Landon, 1974, vol. 2, pp. 441-42.
38. S. Sun and G.R. Belton: *Metall. Mater. Trans. B*, 1998, vol. 29B, pp. 137-45.
39. H.J. Grabke: *Iron Steel Inst. Jpn. Int.*, 1989, vol. 29, pp. 529-38.
40. H.J. Grabke, V. Leroy, and H. Viefhaus: *Iron Steel Inst. Jpn. Int.*, 1995, vol. 35, pp. 95-113.
41. K.C. Mills and B.J. Keene: *Int. Mater. Rev.*, 1987, vol. 32, pp. 1-120.
42. T. Wolkenstein: *Adv. Catal. Relat. Subj.*, 1960, vol. 12, pp. 189-264.
43. W.M. Mullins: *Surface Sci. Lett.*, 1992, vol. 262, pp. L144-L146.