

Kinetics of CO-CO₂ Reaction with CaO-SiO₂-FeOx Melts

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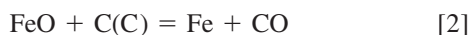
Measurements of the rate of interfacial reaction between CO₂-CO mixtures and CaO-SiO₂-FeOx slags have been made using the ¹³CO₂-CO isotope exchange technique. Ranges of slag compositions from 0 to 100 wt pct 'FeO' and CaO/SiO₂ between 0.3 and 2.0 were examined in the experiments. For each slag, the dependence of the apparent rate constant on temperature and equilibrium oxygen potential was studied. The relationship between the rate constant and oxygen potential was found to be in the form $k_a = k_a^0(a_o)^{-\alpha}$. The parameter a , with values between 0.5 and 0.9, was dependent on the slag composition. The activation energy of the reaction was independent of iron oxide content and dependent on slag basicity.

I. INTRODUCTION

THE reaction of iron oxide dissolved in liquid slag with solid carbon or carbon from a metal bath has been paid considerable attention for its application in various metallurgical processes. In the new generation of iron making processes, for example, Corex and AISI, iron is produced by reduction of iron oxide in slag and carbon, both in solid form and dissolved in the iron bath. Modern electric arc furnaces employ the reaction to induce slag foaming, thereby increasing efficiency of the furnace.^[1,2,3] With a different purpose, iron oxide is reduced by injected carbon in the "slag cleaning" stage of copper making processes. By this means, reduction of magnetite in the slag lowers the slag viscosity, and consequently, physical entrapment of copper matte in the slag is reduced.^[4,5] Driven by such important applications, many studies have been carried out on the reduction of iron oxide in the liquid state by carbon. Depending on the initial and final oxidation state of iron, the overall reaction can be expressed as



or

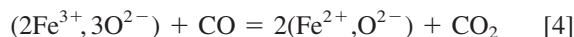


There is a general agreement that the reaction initiates by direct contact of carbon and slag. However, the role of generated CO in the continuation of reaction has been a matter of argument for years. In their study of the rate of FeO reduction, Sugata *et al.*^[6] concluded that the reaction proceeds mainly by direct contact between carbon and the slag. This conclusion has been confirmed by Bafghi *et al.*^[7] who studied the kinetics of FeO reduction by graphite, while simultaneously removing CO by vacuum.

On the other hand, it has been argued by Davies *et al.*^[8] that the reaction area between carbon and slag is not large enough to offer significant reaction rate compared to the measured rates for the reaction. The suggested alternate reaction mechanism is generation and maintenance of a gas layer, composed of mainly CO and CO₂ around carbon particles. The continuation of reaction may occur by CO reduction,

with a much greater contact area with slag, compared to that of carbon particles. The latter mechanism has been proved by direct observations of reaction through slag, by methods such as X-ray fluoroscopy.^[8-15] Having considered the role of intermediate gas layer, separating FeOx containing slag from carbon bearing particles or droplets, there is general agreement^[13-18] that the overall reaction involves the following individual steps in sequence:

- (1) liquid-phase mass transfer of FeOx (Fe²⁺/Fe³⁺ and O²⁻ ions) from the bulk slag to the slag-gas interface;
- (2) interfacial chemical reaction at the slag-gas interface,



- (3) diffusion of CO₂ away from the slag-gas interface toward the gas-carbon interface;
- (4) chemical reaction at the carbon-gas interface,



- (5) diffusion of CO away from the gas-carbon interface to the gas-slag interface.

There are number of consistent findings confirming that in low iron oxide containing slags, mass transfer of iron oxide, *i.e.*, step 1, is more likely to control the overall rate^[14,15,19-24]. In high iron oxide containing slags, carbon gasification or interfacial reaction between gas and slag or a combination of both reactions may act as the rate-limiting step.^[17,24-25] On the other hand, calculations of the rate of gas-phase mass transfer^[13] have shown that the rate of these stages, *i.e.*, 3 and 5, are much higher than the measured overall reaction rate. Therefore, they are ruled out as the rate-limiting step(s).

Different theoretical or empirical kinetic models have been suggested by many authors for the calculations of the rate of each individual stage of the reaction. Nevertheless, a comprehensive kinetic model, enabling us to evaluate the rate at different conditions, has not been successful so far. An overall kinetic model for the rate calculation will require data to evaluate the rate of individual reactions steps.

A. Slag-phase Mass Transfer of FeOx (Step 1)

Knowledge of mass transfer in the liquid phase has been well established over the years, and it is possible to obtain mass-transfer rates, considering transport phenomena. Bafghi

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et al.^[22] successfully showed that it is possible to calculate the rate of mass transfer of oxygen in the slag, by making use of models relating slag chemistry to physical properties. Such models relating slag properties to the mass-transfer coefficient have also been developed by other authors.^[25,26,27]

B. Carbon Gasification (Step 4)

Reaction of CO₂-CO with carbon has been the subject of considerable number of studies.^[28–32] Turkdogan has made a great contribution to the development of kinetic models for this reaction. Recently, he gave a detailed description of the reaction kinetics with different carboneous materials.^[31] Story and Fruehan^[32] also reported the kinetics of reaction of carboneous materials with CO₂ and H₂O. The extent of knowledge about these reactions is sufficient for one to re-evaluate the reaction rate for given experimental conditions.

C. Gas-Phase Mass Transfer (Steps 3 and 5)

Even though gas-phase mass transfer is less likely to act as a rate-limiting step, evaluation of the rate of reaction is simply possible by taking into account the good models involving gaseous diffusion.

D. Interfacial Chemical Reaction between CO-CO₂ and Slag (Step 2)

Numerous kinetics studies have concentrated on understanding the kinetics and mechanism of reaction of CO and CO₂ with iron oxide in the slag. Several profound reviews have been given by Nagasaka *et al.*,^[33] Jahanshahi and Sun,^[34] and Belton^[35] on the topic of gas-liquid slag reaction kinetics. Many aspects of the reaction have been studied and empirical relationships have been reported about the dependence of the rate constant on the slag chemistry. Nevertheless, significant inconsistencies have been reported in the magnitude of reaction rate as well as reaction mechanism. For example, regarding the effect of iron oxide concentration on the rate, there are conflicting results; on one side, El-Rahaiby *et al.*^[36] and Nagasaka *et al.*^[37] showed that for slags of equimolar CaO and SiO₂, the rate was independent of 'FeO' content in the melt with low to rich iron oxide content. On the other hand, Li and Ratchev^[38] and Mori *et al.*^[39] have shown that the effect of iron oxide content on the rate constant can be quite significant. Discrepancies also exist regarding the degree of dependency of the rate constant on the oxidation degree of the melt and slag basicity. Therefore, anyone wishing to develop a kinetic model to take into account all relevant parameters may find it impossible. The problem arises from the complex dependency of rate constant on the slag composition (FeOx content, degree of oxidation of iron in the slag, *i.e.*, Fe²⁺/Fe³⁺ and basicity). Developing an empirical relationship is almost impossible, since it would involve countless numbers of experiments at very precisely controlled conditions. On the other hand, developing a theoretical relationship that matches experimental results has been unsuccessful, mainly due to lack of basic knowledge regarding the true mechanism of the reaction.

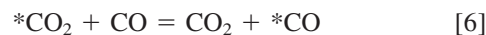
The objectives of the present study were to clarify more aspects of reaction kinetics and mechanism by understanding the inter-relationship between the rate-affecting parameters.

The dependency of the rate constant on four separate variables, temperature, oxygen potential in the gas, iron oxide content in the slag, and bulk slag composition, were studied in the course of experiments. Explanation of dependences involves detailed understanding of the mechanism of reaction, which correspondingly, will require reliable and consistent kinetic data. In the present article, we attempt to draw such kinetic figures that will be used in a subsequent article for explanation of the reaction mechanism. This is in turn aimed at forming the basis of a comprehensive kinetic model for the FeOx reaction in the slag with oxidizing/reducing gases.

II. EXPERIMENTAL DETAILS

A. Theory of Isotope Exchange Method, with ¹³C Tracer Isotope

In the present work, the isotope exchange method, using a 13-carbon tracer isotope, was applied for the measurements of rate of reaction. As pioneers, Belton and his co-workers developed the application of the isotope exchange method in studying kinetics of gas-slag/metal reactions. In the last 3 decades, the technique has been employed to measure the interfacial rate of CO or CO₂ dissociation on the surface of different slags^[35,36,39–44] and metals.^[45–49] The overall exchange reaction is given by



The labeled carbon isotope indicated * can be either the radioisotope ¹⁴C or stable isotope ¹³C. The first-order rate of *CO₂ dissociation (*CO formation) per unit area can be expressed as

$$\frac{dn_{^*\text{CO}}}{A \cdot dt} = \vec{k}_a [P_{^*\text{CO}_2} - P_{^*\text{CO}}(P_{\text{CO}}/P_{\text{CO}_2})_{eq}] \quad [7]$$

where A is the reaction area (cm²) and \vec{k}_a in units of (mol O cm⁻² s⁻¹ atm⁻¹) is the apparent rate constant of forward reaction.

Equation [8] was employed by Cramb *et al.*^[45] to determine the apparent rate constant of CO₂ dissociation when ¹⁴CO₂ is the tracer isotope:

$$\frac{\dot{V}}{ART} \frac{1}{1 + \beta} \left[\frac{1}{1 - P_{^{14}\text{CO}}/(P_{^{14}\text{CO}})_{eq}} \right] = \vec{k}_a \quad [8]$$

where R is the gas constant (cm³ atm mol⁻¹ K⁻¹), T is the absolute temperature (K), β is the equilibrium CO₂/CO ratio, \dot{V} is the volume flow rate of the gas mixture (cm³ s⁻¹), $P_{^{14}\text{CO}}$ is the partial pressure of tagged CO in the reacted gases (atm), and $(P_{^{14}\text{CO}})_{eq}$ is the partial pressure of labeled CO (atm) if complete equilibrium were to be achieved.

In the present study, the stable isotope ¹³C (¹³CO₂) was employed as the tracer isotope. Unlike ¹⁴C, ¹³C has a significant natural abundance; therefore, taking the natural abundance of ¹³C into account, Eq. [8] must be modified as

$$\frac{\dot{V}}{ART} \frac{1}{1 + \beta} \left[\frac{1 - P_{^{13}\text{CO}}^o/(P_{^{13}\text{CO}})_{eq}}{1 - P_{^{13}\text{CO}}/(P_{^{13}\text{CO}})_{eq}} \right] = \vec{k}_a \quad [9]$$

Compared to Eq. [8], the new term $P_{^{13}\text{CO}}^o$ in Eq. [9] is the partial pressure of ¹³CO in the inlet gases.

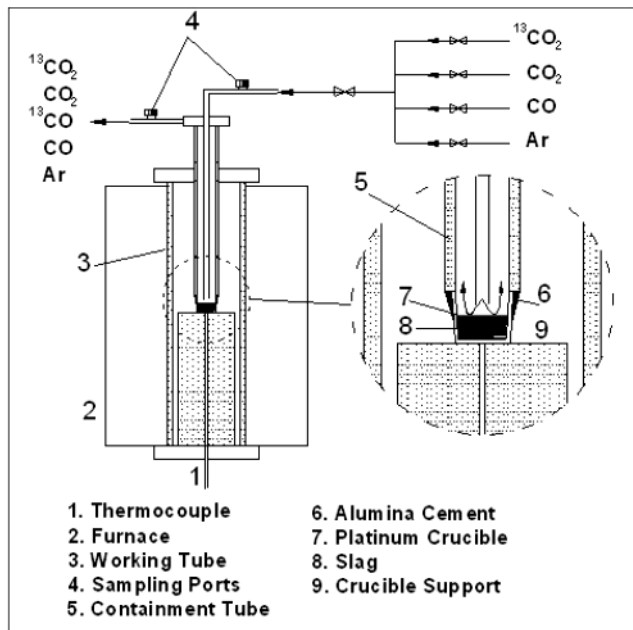


Fig. 1—Schematic diagram of the experimental arrangement.

B. Experimental Setup and Materials

The experimental arrangement is shown schematically in Fig. 1. Two modifications compared to the previously reported experimental method^[44] were applied, which allow more precise determination of the rate constant. First, all the experiments previously carried out in alumina and zirconia crucibles were repeated in a platinum crucible. Second, the conventional method of maintaining the reaction area, *i.e.*, immersion of gas conducting tube in the melt, was replaced with a new method; the platinum crucible was attached to alumina tube by alumina paste. Wetting and creeping of the melt up to tube wall were eliminated, as was dissolution of the alumina tube in the melt. This guaranteed a constant surface area and slag composition. To investigate the effect of the very small exposed area of platinum above melt on the rate of isotope exchange, the previous experiments in the zirconia crucible were repeated by this new setup. Results are provided in Fig. 2.

Slag samples were prepared by premelting reagent grade CaO, SiO₂, and Fe₂O₃ powders in a high-temperature muffle furnace in air. The molten slag was quenched and ground to fine powder. A small sample 0.5 to 1 g was loaded into a 12-mm-diameter platinum crucible. A vertical resistance heated tube furnace, with an 80-mm-diameter alumina working tube, was used for heating and melting the slag samples. All tube ends were fitted with water-cooled stainless steel caps. Deoxidized dry argon was passed through the inside of the working tube to prevent any air ingress into the reaction tube. Temperature was controlled automatically by a programmable EURO THERM Controller. The sample was placed in the hot zone of the furnace, where a temperature variation of ± 1 °C was measured in a zone almost 40 mm in height. A type-B (Pt-6 pct Rh/Pt-30 pct Rh) thermocouple was stuck to the bottom of the crucible to measure the temperature.

Once the desired temperature was achieved, a CO-CO₂ gas mixture was passed down a 5-mm i.d. alumina tube to within 5 mm of the surface of the melt. Gas flow rates were

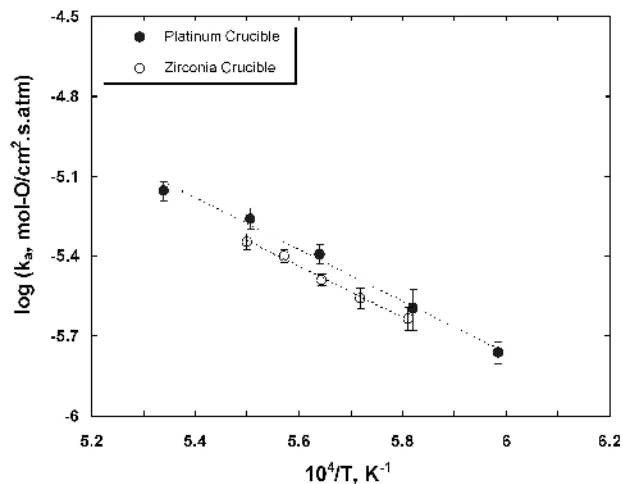


Fig. 2—Arrhenius plot of the apparent rate constant for melts with CaO/SiO₂ = 1 and 30 wt pct 'FeO', at fixed CO₂/CO = 1.0.

adjusted using digital mass flow controllers to yield the preferred CO₂/CO ratio and flow rate. The overall gas flow rate was high enough for interfacial chemical control, rather than gas-phase mass transport. Each slag sample was equilibrated for 1 hour under controlled CO₂/CO ratio before labeled gas was introduced. By decreasing the flow rate of CO₂, the overall CO₂/CO ratio was kept unchanged on introduction of labeled gas. Another 15 minutes was then given to ensure the stable flow of labeled gas. The labeled gas bottle contained 10 mol pct ¹³CO₂, but was diluted on mixing with the main CO₂ gas stream. An Isoprime isotope ratio mass spectrometer (micromass) coupled with gas chromatograph was employed to measure the concentration of labeled species in both ingoing and outgoing gas samples.

III. RESULTS

In order to evaluate the role of each individual parameter on the rate of reaction, a complete set of experiments was designed. The dependence of the apparent rate constant (k_a) on temperature and CO₂/CO ratio was examined for ternary CaO-SiO₂-FeO slags. Gas flow rates of 450 to 600 N cm³/min were applied in order to eliminate mass-transfer resistance in the gas.

A. The Effect of Iron Oxide Content

At unit molar basicity (CaO/SiO₂ = 1), a complete range of iron oxide, from 0 to 100 wt pct 'FeO', was covered by experiments. In each experiment with fixed 'FeO' content, the imposed CO₂/CO varied about 30 to 50 fold, in a range where the risk of formation of metallic iron was eliminated. Temperature dependence of the rate constant was also studied for each single melt. The range of temperature variation was chosen to be above the melting point of the slag. However, for the sake of comparison, the rate constant was measured for most of conditions at a common temperature of 1773 K.

Fig. 3 shows the dependence of the apparent rate constant on the iron oxide content expressed as 'FeO' wt pct at 1773 and 1873 K. The extrapolated values at 1873 K were calculated from values measured at 1773 K, using an activation energy obtained for the same slag. These values

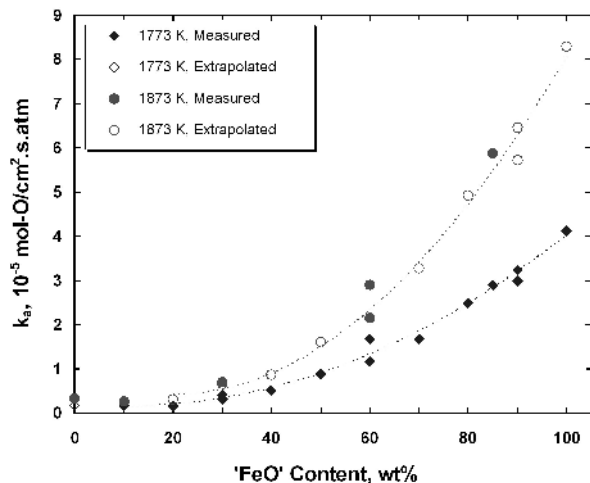


Fig. 3—Dependence of the apparent rate constant at unit CO_2/CO and CaO/SiO_2 on the iron oxide content at 1773 and 1873 K.

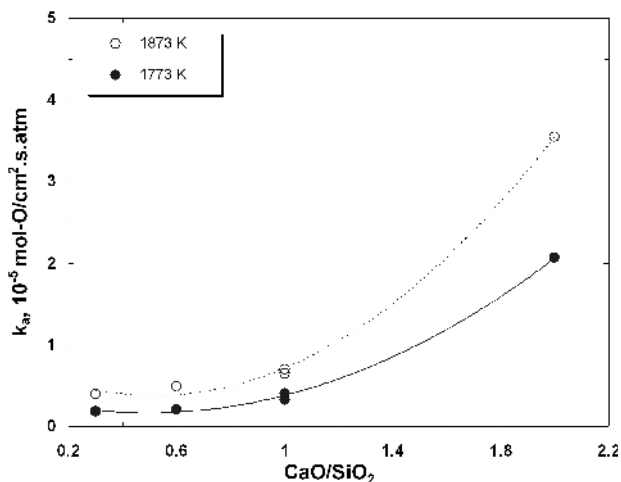


Fig. 4—The dependence of the apparent rate constant at unit CO_2/CO on the CaO/SiO_2 at 30 wt pct FeO.

are represented by open circles in Fig. 3. At both temperatures, k_a increases exponentially with iron oxide content.

B. The Effect of Bulk Slag Composition

A second series of experiments was conducted at constant iron oxide content, 30 wt pct 'FeO', and molar binary basicity (CaO/SiO_2) varying between 0.3 and 2.0. Similar to the previous set of experiments, dependence of the rate constant on oxygen potential and temperature was also examined for each melt.

The dependence of the rate constant on the slag basicity is shown in Fig. 4. It can be seen that k_a increases approximately exponentially with basicity.

C. The Effect of Oxygen Potential

The dependence of the apparent rate constant on the imposed CO_2/CO for some melts is presented in logarithmic form in Fig. 5. The data show excellent agreement with a linear relationship between $\log k_a$ and $\log (\text{CO}_2/\text{CO})$. The slopes of such lines increases with increasing 'FeO'.

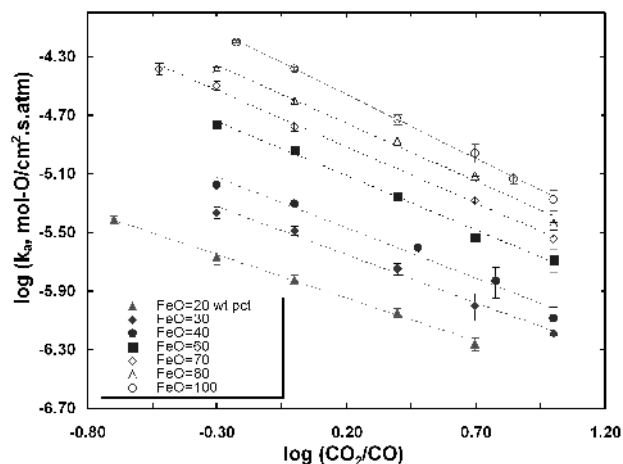


Fig. 5—Apparent rate constant as a function of the equilibrium CO_2/CO ratio for different slags, at 1773 K.

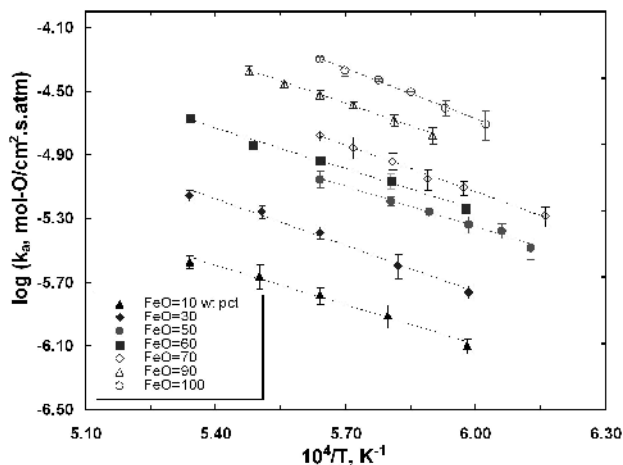


Fig. 6—Arrhenius plot of the apparent rate constant measured at $\text{CO}_2/\text{CO} = 1.0$ for some melts.

D. The Effect of Temperature

The temperature dependence of the apparent rate constant was investigated at unit CO_2/CO for all slag samples. The results for some melts are depicted in Fig. 6. The slope of the Arrhenius plot is essentially constant for all iron oxide contents at unit CaO/SiO_2 . Only the pre-exponential term changes with 'FeO' content.

IV. DISCUSSION

Temperature dependency of the apparent rate constant for dissociation of CO_2 on slag with 30 wt pct 'FeO' at unit CaO/SiO_2 and fixed $\text{CO}_2/\text{CO} = 1$ is shown in Fig. 2. The results are compared for two cases: first, a platinum crucible is attached to the gas conducting tube; and second, a zirconia crucible is used and the alumina tube is immersed in the melt in order to maintain the reaction area. The absolute values of the apparent rate constant measured with the former method are about 10 pct higher. The observed differences between experiments with platinum and zirconia crucibles

are small enough to assure that the small exposed area of the platinum crucible does not have an appreciable effect on the rate of isotope exchange. It was therefore decided that the small error introduced by exposed platinum was more readily accommodated than the inconsistency of surface area caused by variable slag/crucible wetting.

A. The Effect of Oxygen Potential on the Apparent Rate Constant

A series of recent studies^[36,40–42,51] have found that the rate law

$$v = k_a^{\circ}(P_{\text{CO}_2} \cdot a_{\text{O}}^{-\alpha} - P_{\text{CO}} \cdot a_{\text{O}}^{1-\alpha}) \quad [10]$$

closely describes the rate of oxygen exchange between several iron oxide containing melts and CO-CO₂ mixtures. The k_a° (mol O cm⁻² s⁻¹ atm⁻¹) in Eq. [10] is a temperature-dependent constant for a given slag composition; a_{O} is the oxygen activity of the melt, defined by the equilibrium CO₂/CO ratio ($a_{\text{O}} = (P_{\text{CO}_2}/P_{\text{CO}})_{\text{eq}}$ with standard state CO₂/CO = 1); and α is an empirical parameter that quantifies the degree of dependence of the rate constant on the oxygen potential.

The apparent rate constant of oxidation, k_a^{oxi} , and reduction, k_a^{red} , of the melt in CO-CO₂ atmospheres may be derived from Eq. [10] as

$$k_a^{\text{oxi}} = k_a^{\circ} (a_{\text{O}})^{-\alpha} \quad [11]$$

$$k_a^{\text{red}} = k_a^{\circ} (a_{\text{O}})^{1-\alpha} \quad [12]$$

The experimental results of the present study, provided in Fig. 5, show that the rate constant for oxidation of different slags follows Eq. [11] over the range of experimental conditions. The dependence of α on the iron oxide content of the melt is shown in Fig. 7. Values of α start from around 0.5 at low FeOx containing melts to about 0.9 at iron-rich slags and follows the form

$$\alpha = 0.004 \times \text{pct FeO} + 0.5088 \quad [13]$$

There is no systematic study in the literature on the relationship between α and slag composition, but the parameter, α , has been measured for some melts by different

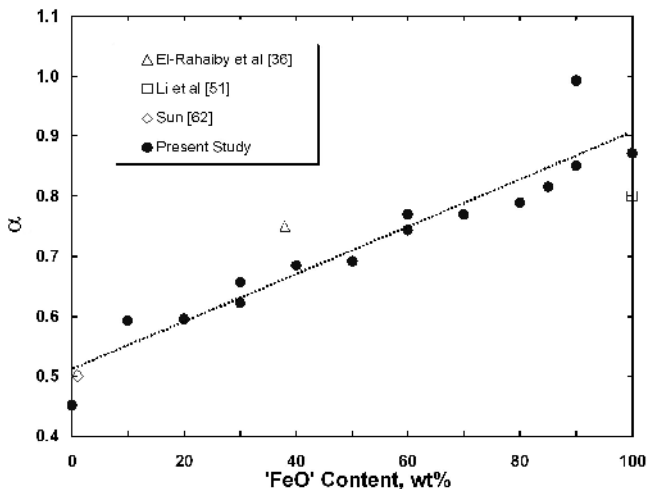
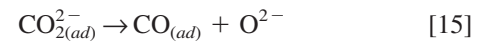
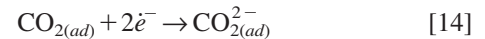


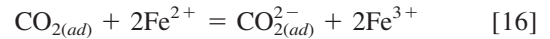
Fig. 7—Degree of dependence of the apparent rate constant on the oxygen potential, α , as a function of iron oxide content.

authors,^[36,39–42,50,51] showing large scatter, sometimes for identical melts. For example, Sasaki *et al.*^[40] have reported values of α being 1.05 and 0.9 for pure iron oxide at 1693 and 1773 K, respectively. The value is inconsistent with $\alpha = 0.8$, measured by Li *et al.*^[51] for iron oxide at 1773 K. Data obtained in similar experimental conditions to the present study are included in Fig. 7.

Sasaki *et al.*^[40] suggested a “charge transfer model” in order to explain the inverse relationship between the apparent rate constant and oxygen potential. Only a brief description is given here. Dissociation of CO₂ at the surface of an ionic melt will ultimately involve transfer of charge, since oxygen exists in the melt as charged ion rather than neutral molecule or atom. Assuming the intermediate complex in the reaction is a doubly charged CO₂ ion (CO₂²⁻), the introduction of oxygen ions (O²⁻) into melt involves the elementary reactions



The surface concentration of CO₂²⁻ ions, $\Gamma_{\text{CO}_2^{2-}}$, is obtained by considering the redox equilibria expressed as



Assuming adsorbed CO₂ to be in equilibrium with CO₂ in gas phase, Eq. [16] yields $\Gamma_{\text{CO}_2^{2-}}$ as

$$\Gamma_{\text{CO}_2^{2-}} \propto P_{\text{CO}_2} (\text{Fe}^{2+}/\text{Fe}^{3+})^2 \quad [17]$$

Assuming that either Reaction [14] or [15] acts as the rate-controlling step, the rate law for the forward reactions is expressed by

$$v = kP_{\text{CO}_2} (\text{Fe}^{2+}/\text{Fe}^{3+})^2 \quad [18]$$

where k is the rate constant for the forward reaction, for a given number of reaction sites. Considering Reaction [4], redox equilibria of iron ions in equilibrium with CO-CO₂ gives

$$(\text{Fe}^{2+}/\text{Fe}^{3+}) \propto (\gamma_3/\gamma_2) \cdot (\text{CO}/\text{CO}_2)^{0.5} \quad [19]$$

where γ_2 and γ_3 are activity coefficients of ferrous and ferric ions, respectively. Over the range of composition where the ratio of γ_3/γ_2 remains “ideally” constant, the rate constant equation (Eq. [11]) can be obtained with ideal α equal to 1. It was observed from the results of the present study that the value of α deviates from unity and the extent of deviation varies for different iron oxide contents. Deviation from $\alpha = 1$ may have four possible causes.

1. Redox equilibria of iron oxide does not follow ideal behavior

If the ratio of γ_3/γ_2 depends on the oxidation state of the slag, then redox equilibria can be approximated by a relationship of the form^[52–57]

$$(\text{Fe}^{2+}/\text{Fe}^{3+}) \propto (\text{CO}/\text{CO}_2)^\beta \quad [20]$$

where the value of β differs from 0.5 (ideal value). Assuming that transfer of two charges is the only mechanism by which oxygen potential affects the rate, then α must be equal to

2β . In Table I, the values of α and 2β for some melts are gathered from the literature. For some slags, a close relationship to $\alpha = 2\beta$ is followed. However, for many other experimental conditions, the relationship does not hold. For example, Tran *et al.*^[50] found that for 28.9CaO-54.5SiO₂-7.2MgO-10FeOx (wt pct) slag, $\alpha = 0.62$, while for the same slag, $\beta = 0.495$. It may be concluded that the deviation of γ_3/γ_2 from unity may not be the only reason for which dependence of the rate constant on oxygen potential deviates from “ideal” behavior.

2. Transfer of single charge in the rate-controlling step reaction

Grabke and Viehhaus^[58] have discussed that dissociation of CO₂ on the surface of solid wustite may involve formation of singly or doubly charged CO₂ ions. Assuming that the introduction of oxygen ions into the iron oxide melt may involve formation of single charge CO₂ ions CO_{2(ad)}⁻ instead of double charge ions (CO_{2(ad)}²⁻), dissociation of CO_{2(ad)} can be further broken into two elementary reactions:



Assuming that transfer of one charge, *i.e.*, Reaction [21], controls the overall rate, over the range of constant γ_3/γ_2 , the rate law yields

$$k_a^{oxi} = k_a^o (a_o)^{-0.5} \quad [23]$$

Therefore, it may be discussed that the mechanism of the reaction can be formation of singly or doubly charged CO₂ ions or a combination of both. Values of α varying between 0.5 and 1 may be then related to the relative stability of intermediate complexes CO₂⁻ and CO₂²⁻ at different conditions. At this stage, the state of knowledge is not sufficient to evaluate the relative stability of each ion at high temperatures on different surfaces.

3. Change in the surface structure of the slag

With variation in the oxygen potential, changes occur in the oxygen content of the melt, as well as the ratio of ferric and ferrous ions. This in turn may affect the rate, theoretically from two sources: blockage of reaction sites or change in the electronic structure of the surface.

Dependence of the rate constant on oxygen potential due to surface adsorption of oxygen has been reported for

Table I. Degree of Dependence of the Apparent Rate Constant (α) and Fe³⁺/Fe²⁺ (β) on the Equilibrium Oxygen Potential

Slag	α	2β
Pure FeOx	1.05 ^[40] (at 1693 K) 0.9 ^[40] (at 1773 K) 0.8 ^[51] 0.87 (present study)	1.0 ^[52]
Calcium ferrite (24 mol pct CaO)	0.79 ^[42]	0.83 ^[53]
Equimolar CaO-SiO ₂ -FeOx	0.75 ^[36]	0.68 ^[54] 0.80 ^[55]
Silica saturated iron silicate CaO-SiO ₂ -5 wt pct FeO, (CaO/SiO ₂) = 1	1.0 ^[36] 0.84 ^[36]	1.0 ^[56] 0.9 ^[57]

nickel,^[45,47] iron,^[46] copper,^[48] and solid wustite.^[58] However, Grabke and Viehhaus^[58] found that for wustite, adsorption occurs, only at temperatures lower than 1073 K. The surface structure of oxide melts at high temperature and dependence on oxygen potential has not yet been fully understood. Measurements by Gaskell and his group^[59,60] on liquid iron oxide at 1673 K showed that the surface tension of liquid iron oxide is approximately constant with Fe³⁺/Fe²⁺. Therefore, it is reasonable to consider negligible adsorption of oxygen or segregation of other ionic species to the surface. Thus, the influence on α of change in the surface constituents is likely to be minor.

4. Uncertainty in the experimental measurements

The measurement of kinetic parameters at high temperature may involve random and systematic errors. One of the greatest problems is maintaining a fixed reaction area over the course of an experiment. Many factors can affect the reaction area, even for a single experiment. Change in the oxygen potential, for instance, may affect the wetting of the containment tube or crucible that changes the curvature of the surface. Melt splashing or formation of a crater under high gas flow rate may also occur. These phenomena result in different areas at different conditions. Dissolution of the containment tube or crucible changes the composition of the melt, especially in longer experiments. Also, intentional changes in the temperature or oxygen potential or unwanted fluctuations in the gas flow rates affect the measurements. The sources of error are countless and sometimes inevitable. As discussed earlier, in some cases, even for similar experimental conditions, various authors obtained quite different values for the rate and kinetic parameters such as α . In the present study, the authors believe there is sufficient consistency in the data to assure the variation of α does not arise from experimental uncertainty. This is evidenced by the extremely consistent behavior shown in Fig. 5 and 7.

B. The Effect of Iron Oxide Content on the Apparent Rate Constant

Fig. 8 shows the dependence of the apparent rate constant on the iron oxide content. Clearly, increasing iron oxide

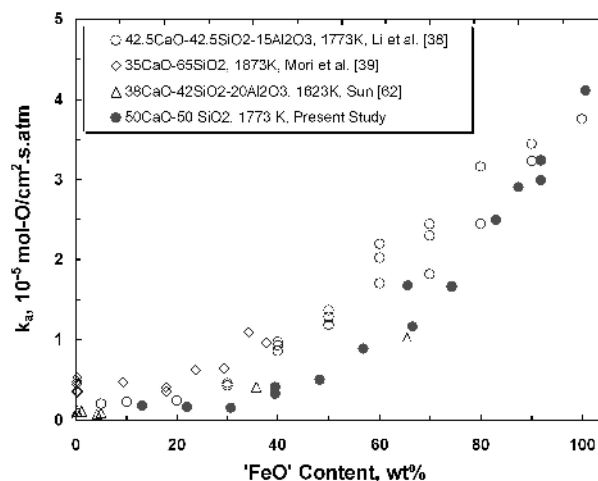


Fig. 8—Apparent rate constant of oxidation and reduction reaction as a function of iron oxide content, at unit CO₂/CO.

content up to 30 wt pct does not have a significant impact on the rate. With the increase in iron oxide content from 30 to 100 pct, the rate increases dramatically. Within experimental error, the dependence can be represented by an exponential function. Results of the rate constant from some other publications are also provided in Fig. 8. The results from the present study are in close agreement with the values of rate constants measured by Li and Ratchev^[38] using a thermogravimetric technique. The slag basicity in their study was identical to the present work, but their master slag contained 15 wt pct Al₂O₃. Larson and Chipman^[61] found that addition of Al₂O₃ to liquid iron oxide does not change the Fe³⁺/Fe²⁺ ratio, so it may be treated as a neutral dilutant of a basicity of unity. Two other studies by Sun^[62] and Mori *et al.*,^[39] for low iron oxide containing slags, show similar dependency between the rate and iron oxide content. The differences in the absolute values of rate constant in Fig. 8 may be attributed to the difference in temperature and slag basicity.

Despite good consistency in the measurements presented in Fig. 8, not all studies agree on the same dependency of the rate constant on iron oxide content. For example, El-Rahaiby *et al.*^[36] have reported that for calcium iron silicate slags with basicity of 1, changing iron oxide content in the range of 5 to 100 wt pct does not affect the rate constant. Fine *et al.*,^[63] on the other hand, reported that the rate of reduction of FeO from slag by CO is directly proportional to the activity of FeO, in the slags with less than 48 wt pct FeO. In slags containing between 48 and 68 wt pct, the rate was constant with respect to FeO content. The kinetics of the iron oxide reduction to metallic iron in slags of equimolar CaO and SiO₂ has also been examined by Nagasaka *et al.*^[37] Their results have shown that the rate is independent of FeO concentration in the range of 35 to 100 wt pct FeO.

As discussed previously, the overall rate of oxidation and reduction of iron oxide by CO-CO₂ is presumably controlled by the rate of elementary Reaction step [15]. The derived rate expression for the forward reaction, Eq. [18], does not explicitly contain the effect of iron oxide. However, one may suppose that at a certain CO₂/CO ratio, increasing FeO content tends to change the Fe³⁺/Fe²⁺ ratio and by this means affects the rate. Fig. 9 shows the variation of Fe³⁺/Fe²⁺ ratio

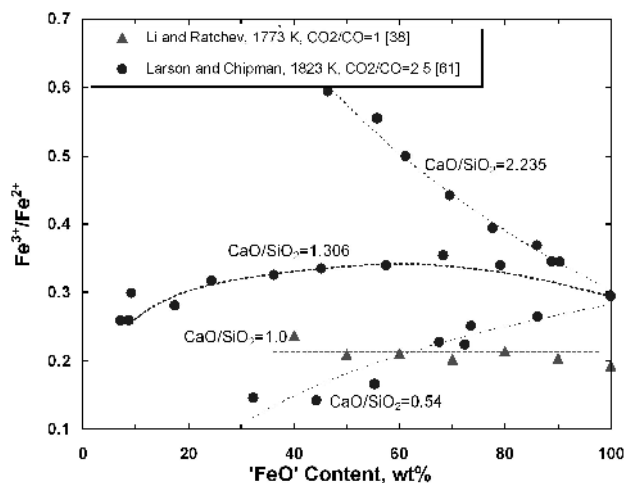


Fig. 9—Ferric/ferrous ratio as a function of iron oxide content for different slags.

with iron oxide content for some slags. The figure includes data obtained by Larson and Chipman^[61] and Li and Ratchev.^[38] It can be seen that the effect of iron oxide content on the ferric/ferrous ratio may not be explained without incorporating the effect of bulk slag composition. At slag basicity greater than unity, iron oxide content decreases the Fe³⁺/Fe²⁺. The dependency becomes weaker in the rich iron oxide slags. The opposite behavior is seen for acidic slags, *i.e.*, CaO/SiO₂ less than unity. Approaching from basic and acidic slags to slags with unit basicity, the effect of iron oxide becomes weaker so that at unit basicity, Fe³⁺/Fe²⁺ becomes essentially independent of the iron oxide content. The results in Fig. 9 are for high iron oxide content slags. For slags containing less than 10 wt pct FeO, discrepancies exist on the role of FeO content on the Fe³⁺/Fe²⁺ ratio. Jahanshahi and Wright^[64] studied the redox equilibria for Al₂O₃-CaO-SiO₂-FeO slags with CaO/SiO₂ between 0.92 and 0.97. They found that Fe³⁺/Fe²⁺ decreased sharply as total iron content increased to 4 to 6 wt pct. Further increase in Fe content up to 24 wt pct did not show a significant effect. Yang and Belton,^[57] on the other hand, were not able to find a measurable dependency in the range of 3 to 10 wt pct FeOx for similar slags. It may be concluded that for slags of unit basicity, Fe³⁺/Fe²⁺ tends to remain constant over the entire range of iron oxide content from about 5 to 100 wt pct. Therefore, the dependence of the rate constant on the iron oxide content in Fig. 8 cannot be related to the changes in the state of oxidation of melt, *i.e.*, Fe³⁺/Fe²⁺.

The effect of iron oxide content on the rate may be explained qualitatively, with regard to charge transfer consideration. Jiao and Themlis^[65] gathered data on the electrical conductivity of iron oxide containing melts. They showed that in the range of 11 to 83 wt pct 'FeO', the electrical conductivity is exponentially proportional to the concentration of 'FeO' in the slag. Narita *et al.*^[66] found similar trend for slags containing ~30 to 65 wt pct FeO. With the charge transfer involved in the reaction mechanism, and also iron oxide showing semiconductor behavior, we may expect that the rate constant and electrical conductivity follow similar trends. The evidence presented previously shows that with increasing 'FeO' content, both conductivity and rate constant increase exponentially. This subject will be discussed in more detail in a subsequent article.

C. The Effect of Slag Basicity on the Apparent Rate Constant

Dependence of apparent rate constant on the slag basicity in the present work is compared in Fig. 10 with results from studies by El-Rahaiby *et al.*^[36] and Mori *et al.*^[39] All results show that increasing basicity increases the rate, considerably.

The effect of nonreacting components of slag on the interfacial reaction rate may be discussed with more clarity by looking at the role of surfactants on the reaction as they concentrate at the surface. Segregation of such species, to the surface of the melt, may "poison" the surface and occupy the available reaction sites. It is thus expected that the addition of surface-active species decreases the apparent rate constant significantly. This is seen to be in agreement with a series of recent findings.^[41,42,43] Sun and Belton,^[41] for example, found that the addition of 2 mol pct P₂O₅ to iron oxide resulted in a depression of the apparent rate constant

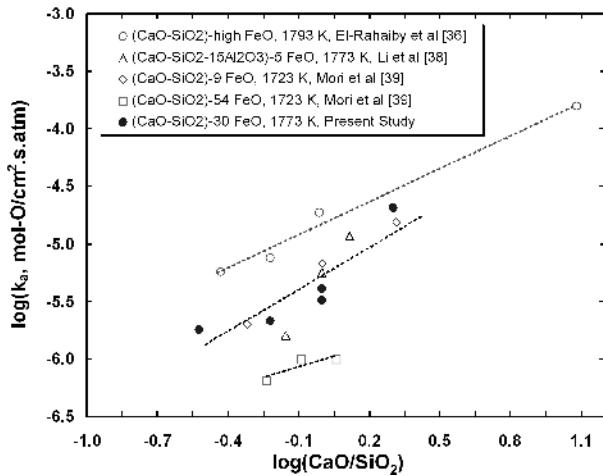


Fig. 10—Dependence of the apparent rate constant on the slag basicity at unit CO_2/CO (FeO in wt pct).

by a factor of 3. Though this mechanism reasonably explains the effect of some acidic surfactants, it failed to describe the effect of basic components, for example, CaO and Na_2O . Application of a site blockage mechanism anticipates that these components also decrease the rate, proportional to their segregated concentration at the surface. However, it has been observed that basic oxides, despite decreasing the surface concentration of FeO, have a positive effect on the rate constant.^[36,38–40,51] Sun and Belton^[41] and Matsura and Tsukihashi^[43] have reported a significant increase of the rate with small additions of basic surface-active Na_2O . Therefore, to explain the effect of slag basicity on the rate, the use of only a site blockage mechanism is insufficient.

The effect of slag basicity on the rate may also be discussed with regard to its effect on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. Fig. 9 shows that at fixed oxygen potential, $\text{Fe}^{3+}/\text{Fe}^{2+}$ increases with basicity. Therefore, with rate Eq. [18], if slag basicity influences the rate by changing $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, the rate constant must decrease with increasing basicity. This is not the case, as observed in Fig. 10.

Again, another approach to explain the influence of basic oxides on the reaction rate and mechanism employs the charge transfer mechanism. With the rate-controlling step given by Reaction [15], the rate of reaction is proportional to the density of free electrons at the surface of the melt. It has been reported^[67] that more basic oxides have a higher Fermi energy, an indication of the electrochemical potential of free electrons. Therefore, the addition of basic oxides is expected to result in a higher availability of electrons for the reaction leading to a higher reaction rate. By this mechanism, basic oxides increase and acidic oxides decrease, the rate in proportion to their segregation at the surface of the melt and their “basic strength.” The theoretical analysis is in agreement with the findings of Li and Ratchev^[51] that addition of stronger basic oxides to the iron oxide has more pronounced effect on the reaction kinetics.

Dependence of α on slag basicity was also examined in the present work. The values of α for slags with molar basicity of 1 and iron oxide content fixed at 30 wt pct are provided in Fig. 11. It is seen that increasing the slag basicity has a slight decreasing effect on the value of parameter α . This dependency may be discussed on the basis of a charge transfer mechanism.

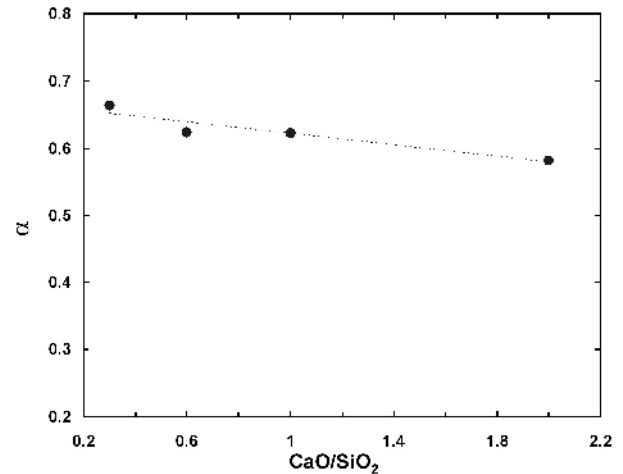


Fig. 11—Dependence of α on slag basicity at ‘FeO’ = 30 wt pct.

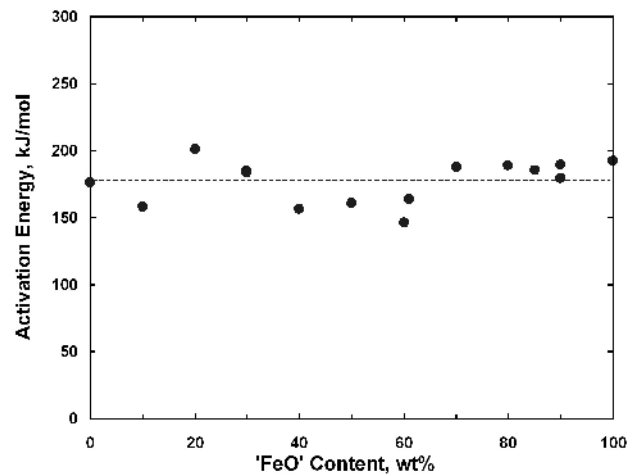


Fig. 12—Measured activation energy at unit CO_2/CO , as a function of ‘FeO’ content, for melts with $\text{CaO}/\text{SiO}_2 = 1.0$.

In terms of making electrons more easily accessible for the reaction, the role of basicity is similar to that of $\text{Fe}^{2+}/\text{Fe}^{3+}$. At fixed iron oxide content, the higher the basicity, the less the effect of iron oxide and thus $\text{Fe}^{2+}/\text{Fe}^{3+}$. Therefore, higher CaO/SiO_2 weakens that dependency of the rate constant on the $\text{Fe}^{2+}/\text{Fe}^{3+}$ on oxygen potential, presumably because basic oxides are an oxygen potential independent source of electron donors.

D. The Effect of Temperature on the Apparent Rate Constant

The activation energies for slags with different iron oxide contents are provided in Fig. 12. It is seen that activation energy at an average value of 178 kJ/mol is essentially independent of the iron oxide content for slags with unit basicity.

Fig. 13 shows that in slags with fixed FeO content, increasing the molar basicity of the slag from 0.3 to 2.0 decreases the activation energy from 197 to 146 kJ/mol. This is in agreement with other findings, showing that addition of basic oxides decreases the activation energy of the reaction. Applying a charge transfer mechanism, this may be explained as follows: the addition of basic oxides strengthens the adsorp-

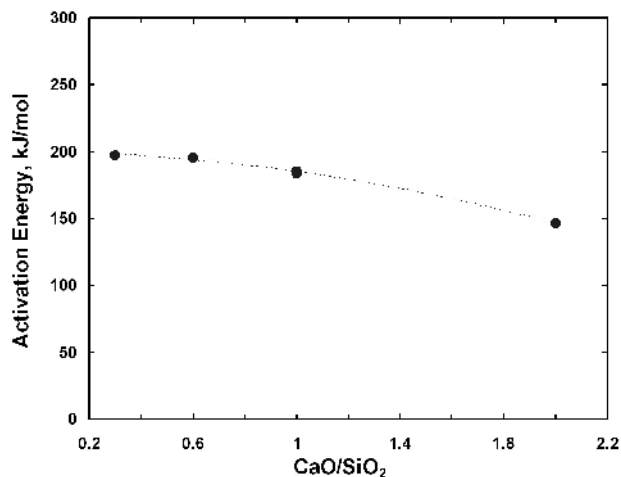


Fig. 13—Activation energy of the reaction at unit CO_2/CO as a function of binary basicity of the slag, for melts with 30 wt pct 'FeO'.

tion of negatively charged CO_2^{2-} ions to the surface of the slag, hence decreasing the required activation energy for formation of complex ion CO_2^{2-} .

The effect of temperature on α was investigated for a slag with unit CaO/SiO_2 and 60 wt pct FeOx. It was observed that the variation of α in the range of 1623 to 1873 K was insignificant. Li *et al.*^[51] also found that $(1 - \alpha)$ for reduction of pure FeO, at 1673 and 1773, is identical at 0.18.

V. CONCLUSIONS

1. The apparent reaction rate constant for dissociation of CO_2 on the surface of $\text{CaO-SiO}_2\text{-FeOx}$ slags increases with FeOx content of the slag, according to $k_a = 0.11 \exp(0.0383 \times \text{pct FeO})$ at 1773 K and $\text{CO}_2/\text{CO} = 1$.
2. The apparent rate constant decreases with increasing the equilibrium oxygen potential, as $k_a = k_a^0 (\text{CO}_2/\text{CO})^{-\alpha}$.
3. The parameter α is dependent on slag composition with a stronger effect of iron oxide content compared to basicity. At unit CaO/SiO_2 , α follows a linear relationship with iron oxide content as $\alpha = 0.004 \times \text{pct FeO} + 0.5088$.
4. The oxygen potential dependence of the apparent rate constant suggests a rate-determining step involving formation of either CO_2^- or CO_2^{2-} , with CO_2^{2-} becoming more significant at higher 'FeO' contents.
5. $\text{Fe}^{2+}/\text{Fe}^{3+}$ and basic oxides are not exactly equivalent as a source of electrons for formation of CO_2^{2-} ; however, further work is required to establish the difference.

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