Relative Rates of H_2O and CO_2 Reaction with Model Bath Smelter Slags

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ABSTRACT

The relative reaction rates of H_2O and CO_2 with bath smelting type slag have been determined by establishing steady state in the slags under impinging jets of H_2O-CO or H_2O-CO-Ar mixtures. Values of the steady state oxygen activity were derived from measurements of the steady state Fe^{3+}/Fe^{2+} ratio. Relative rates of H_2O and CO_2 with these slags were obtained by using the information of steady state oxygen activity and the rate equation at steady state. The results show that the apparent first order rate constant for H_2O dissociation is a few times that for CO_2 dissociation over these slags and the relative rates are a close function of the basicity of the slags.

1. INTRODUCTION

In bath smelting processes, gas mixtures of CO_2, CO, H_2O and H_2 exist above the slag-metal bath, and their proportions depend on pre-reduction rate, post-combustion rate and volatile level of the coal. If a medium volatile coal is used, the H_2O level would be typical of 19-23% after post-combustion[1]. Ferrous iron in the slag can be oxidised to ferric iron, which will use additional reducing agent within the bath. Thus, there is a limit to the degree of achievable post combustion and this will depend, in part, on the rates of reaction of the CO_2 and H_2O with the slag. A knowledge of the relative rates of reaction of CO_2 and H_2O with the slag is therefore important in understanding the interrelationship between maintainable degree of post combustion and the volatile matter content of the coal used in the process.

Belton[2-3] and Nagasaka and Ban-ya[4] have discussed the available information on interfacial reactions of melts containing iron oxide with CO-CO_2. Dissociative chemisorption and associative desorption of CO_2 at the interface appear to be the rate-controlling steps when CO_2-CO gases are involved in reactions with melts.

Nagasaka, et al[5-8] found that the apparent rate constant at iron saturation was a function of the basicity of the melts for liquid Fe_tO, binary and ternary silicate melts containing Fe_tO. In the studies of the rate of dissociation of CO_2 over liquid iron oxide and CaO-saturated calcium ferrites[9], and SiO_2-saturated iron silicates and manganese silicates[10] by the isotope exchange technique, the apparent first order rate constant was found to be inversely proportional to the state of oxidation or Fe^{3+}/Fe^{2+} ratio squared of the melts at a given temperature. The apparent first order rate constant of CO_2 dissociation $(k_a)_C$ was found to follow the equation below for more complex melts - equimolar calcium iron silicates[10], calcium ferrite melts[11-12] and the calcium aluminosilicate melts with "FeO" contents up to 1.5wt% [11], ie,

$$(k_a)_C = k_C\, a_o^{-x} \tag{1}$$

where k_C is a system and temperature dependent rate constant and $-x$ is the slope of the plot of $\log(k_a)_C$ versus $\log a_o$ for CO_2 dissociation.

Kukhtin and Smirnov[13-14] have measured the reduction rate of ferric iron oxide in melts 40%CaO-40%SiO_2-20%Al_2O_3+(0.53-5.70%)Fe_2O_3 by CO at 1350-1450°C. The rate of reduction, claimed to be predominantly governed by the interfacial kinetics. The reduction rate of the slag 41CaO-38SiO_2-21Al_2O_3 (wt%) containing 5.8wt%Fe with a 5%CO-inert gas was observed to be a function of Fe^{3+}/Fe^{2+} ratio of the slag in studies where the slag was stirred by a rotating disc[15].

The kinetic information on reactions with H_2O-H_2 is very limited, and even more insufficient in respect to the relative rate of reactions of CO_2-CO and H_2O-H_2 with such melts. Nagasaka[7] found that the maximum rate for melt 'FeO'-36mol%SiO_2 to be about one order of magnitude higher than the interfacial rate with Ar-CO mixtures[5]. For the melt 41CaO-38SiO_2-21Al_2O_3+5.8Fe (wt%), the reduction rate by H_2 was about 3-6 times that by CO[15]. Glaws and Belton[16] examined the rate of dissociation of H_2O over liquid silica-saturated iron silicates by the isotope exchange technique. It was found that the interfacial rate of reaction of H_2O with the melt was first order with respect to the partial pressure of water vapour, and the apparent first order rate constant was expressed as a function of oxygen activity or the equilibrium Fe^{3+}/Fe^{2+} ratio squared of the melt, as observed for the CO_2-CO reaction with iron silicates[10].

Using a steady state technique, Sasaki and Belton derived the relative dissociation rates of H_2O and CO_2 on liquid silica saturated iron silicates at 1250°C [2,17]. The apparent first order rate constant for the oxidation of the melt by H_2O was observed to be approximately 20 times higher than that by CO_2.

The slags formed in the proposed bath smelting processes are essentially the systems $CaO-SiO_2-Al_2O_3$ and $CaO-SiO_2-Al_2O_3-MgO$ containing iron oxide[18-21]. The principal objective of the present work was to establish the relative interfacial rates of reaction of CO_2 and H_2O with such slags at compositions and temperatures appropriate to the bath smelting processes using the steady state approach technique.

2. EXPERIMENTAL

Slags of the system $CaO-SiO_2-Al_2O_3$ were synthesised with analytical grade chemicals, calcium carbonate, silica, alumina and ferric oxide. Their analysed compositions (wt%) are $35.6CaO-35.1SiO_2-19.1Al_2O_3$ (slag A), $22.2CaO-53.2SiO_2-15.3Al_2O_3$ (slag B) and $40.1CaO-28.3SiO_2-20.3Al_2O_3$ (slag C) containing 5-10wt% Fe_2O_3.

A platinum crucible of 9-10 mm ID and 3 mm in height, holding a slag sample of 0.25-0.30 grams, was suspended by fine platinum wires secured outside of the crucible, as shown in Fig. 1. Exposure of the platinum wire and crucible to gas mixtures was avoided to minimise platinum catalysis on the water-gas shift reaction[22-23]. The crucible was positioned approximately 5 mm below the alumina gas delivery tube of 5 mm ID. This assembly was then inserted into the hot zone of a vertical furnace and exposed to the flowing H_2O-CO mixtures. At the end of the experiment, the quenched samples were chemically analysed to determine Fe^{3+}/Fe^{2+} ratios of the melts.

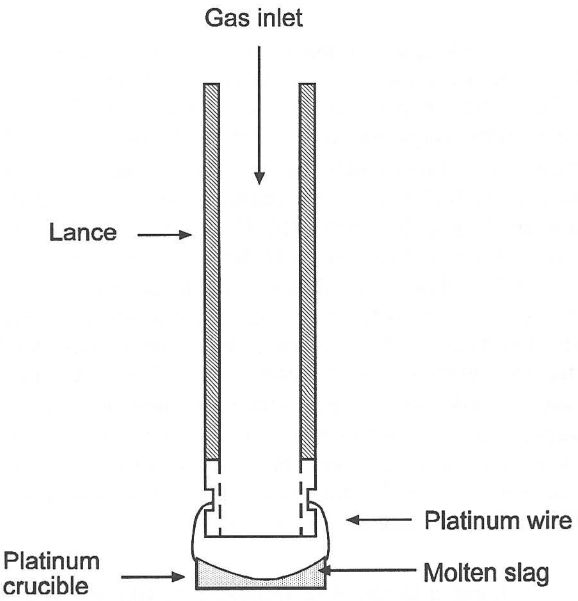

Fig. 1. The crucible assembly used in the steady state measurements.

The two-stage water saturator which was employed to supply mixtures of water vapour and CO, was similar to that described by Belton and Richardson[24]. The appropriate ratio of H_2O/CO was achieved by controlling the water bath temperature, and using argon dilution if necessary. The bath temperature was controlled within a maximum variation of ±0.1°C.

3. RESULTS

In the reactions of H_2O-H_2 and CO_2-CO mixtures with iron oxide-containing melts, the steady state occurs when the rate of oxygen addition to matches that of oxygen removal from the interface.

3.1 Determination of experimental conditions

To determine the approach to steady state, slag A was exposed to H_2O-CO mixtures with the constant H_2O/CO ratio of 1.0 at 1350°C and a flow rate of 520 ml/min, and slag B was exposed to a mixture with an H_2O/CO ratio of 0.4 at 1450°C at a total flow rate of 450 ml/min. The Fe^{3+}/Fe^{2+} ratios were measured as a function of time and the results are plotted in Fig. 2. The Fe^{3+}/Fe^{2+} ratio declines with reaction time from a starting value of above about 5, and appears to reach a plateau after a reaction time of about 30-40 minutes. Reaction times of above 60 minutes were maintained in the subsequent experiments.

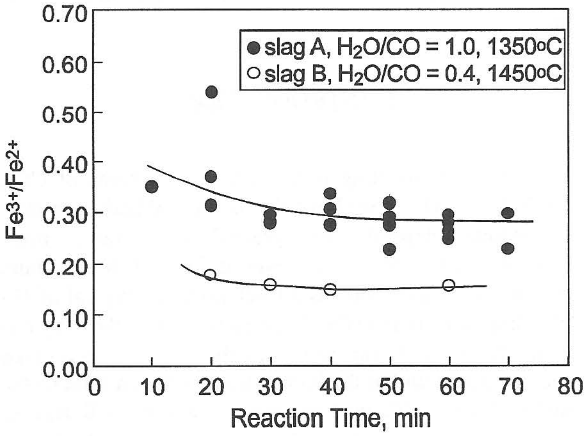

Fig. 2. Approach to steady state for slags A and B.

The total flow rate of $H_2O-CO-Ar$ mixtures was varied at H_2O/CO ratios of 0.5 and 1.0 at 1350°C for slag A. The results are shown in Fig. 3, where it appears that the Fe^{3+}/Fe^{2+} ratio approaches a constant value when the total flow rate is above 300ml/min. In all the studies the total gas flowrate exceeded 500ml/min.

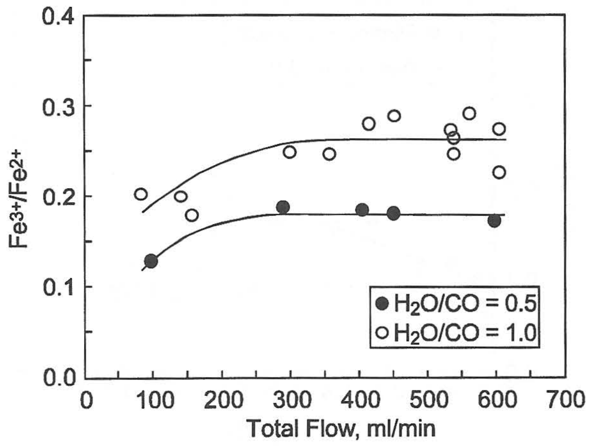

Fig. 3. Influence of the total gas flow rate on values of the steady state Fe^{3+}/Fe^{2+} ratio.

An estimation of the mass transfer coefficient in gas phase was made by Taniguchi's correlation[25-26]. For a gas phase which comprised of H_2O and CO only with an equal partial pressure of 0.5atm and a total gas flow rate of 500ml/min, the estimated mass transfer coefficient is 1.01×10^{-4} $mol/cm^2\cdot sec\cdot atm$, which is about 2 orders of magnitude higher than the expected interfacial rate constant of CO_2-CO reaction in this system[11].

As Ar was used to dilute the gas mixtures to obtain some of the H_2O/CO ratios required, the influence of Ar on the steady state Fe^{3+}/Fe^{2+} ratio was investigated. Slag A was reacted with H_2O-CO-Ar mixtures at different levels of Ar dilution at constant H_2O/CO ratios of 1.0 and 0.5 at 1350°C. The results, as seen in Fig. 4, show that the steady state Fe^{3+}/Fe^{2+} ratio is independent of the Ar partial pressure, even when the Ar dilution is up to 40%, ie., for pH_2O and pCO varying between 0.5 and 0.3 atm.

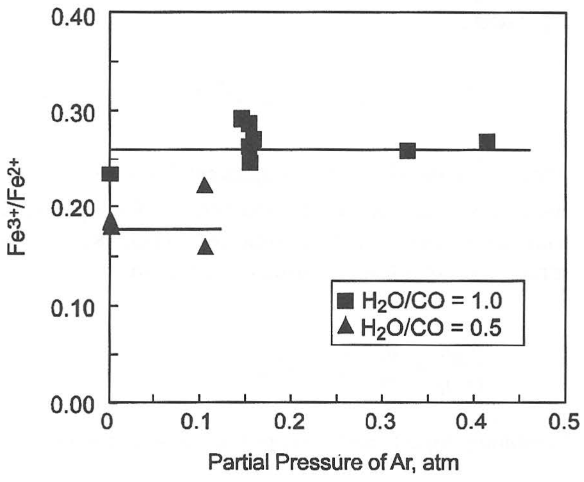

Fig. 4. Independence of the steady state Fe^{3+}/Fe^{2+} ratio on Ar dilution.

3.2 Steady state Fe^{3+}/Fe^{2+} ratio of slags A, B and C

Steady state values of the Fe^{3+}/Fe^{2+} ratio were measured for slag A containing 5 and 10wt% "FeO" at 1350°C. These data are presented in Fig. 5 as a function of H_2O/CO ratio. Within the limits of the experimental scatter the results do not indicate any significant dependence on the total iron oxide concentration.

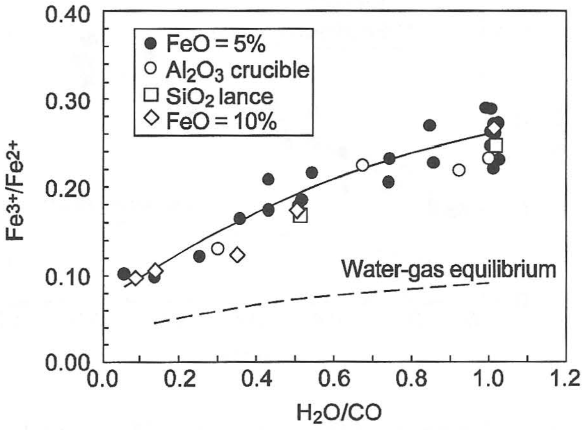

Fig. 5. The steady state Fe^{3+}/Fe^{2+} ratio for slag A in comparison with the equilibrium values at 1350°C.

Also shown in Fig. 5 are a limited number of results obtained using alumina crucibles and silica gas inlet tubes. The replacement of the alumina gas inlet tube by a recrystallised silica tube was made to examine any influence of the lance material on the measurements. Alumina crucibles were used to examine if catalysis of the water-gas reaction was affecting the results due to the exposed outsides of the platinum crucibles. Within the limits of the scatter, these substitutions had no effect.

If the reactions of H_2O-CO mixtures with the melt reach equilibrium, ie., the water-gas reaction $H_2O + CO = H_2 + CO_2$ is in equilibrium, the equilibrium Fe^{3+}/Fe^{2+} ratio is determined by the appropriate correlation[27]. Values of the "equilibrium" Fe^{3+}/Fe^{2+} ratio are indicated by the continuous curve in Fig. 5. The steady state values of the Fe^{3+}/Fe^{2+} ratio increase monatonically with H_2O/CO ratio and, for this slag, are greater than the corresponding equilibrium Fe^{3+}/Fe^{2+} values by a factor of almost 2.5. This appears to be independent of iron concentration over the limited range studied.

Measurements were also carried out at 1300°C for slag A with 10wt% "FeO". The results are compared in Fig. 6 with those at 1350°C. The steady state Fe^{3+}/Fe^{2+} ratios are identical in this narrow temperature change within experimental error.

Measurements were carried out for slag B at the two temperatures 1350 and 1450°C. The results are presented in Fig. 7. The steady state Fe^{3+}/Fe^{2+} ratio is up to a factor of 4 higher than the corresponding equilibrium Fe^{3+}/Fe^{2+} ratio calculated by the appropriate correlation[27]. Within the scatter, there appears to be no effect of temperature on the results.

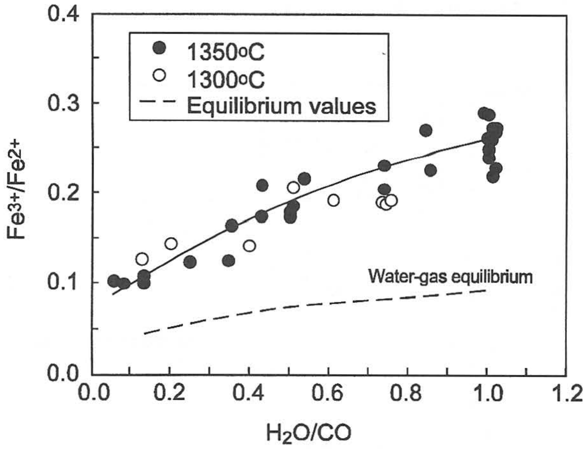

Fig. 6. Comparison of the steady state Fe^{3+}/Fe^{2+} ratios for slag A at 1300 and 1350°C.

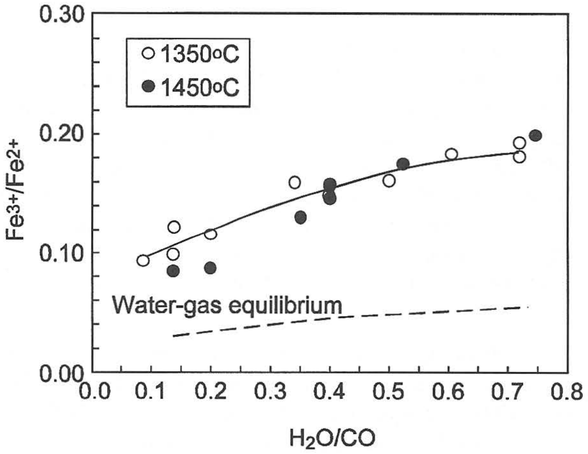

Fig. 7. The steady state Fe^{3+}/Fe^{2+} ratios as a function of H_2O/CO ratio for slag B at 1350 and 1450°C.

The steady state measurements for slag C were carried out at 1500°C. The results are presented in Fig. 8. The steady state Fe^{3+}/Fe^{2+} ratio increases smoothly with the rise of H_2O/CO ratio in gas mixtures. Again, the ratio is higher than the corresponding equilibrium value calculated by the appropriate correlation[27]. The measurements were again verified by using recrystallised alumina crucibles. The results, also shown in Fig. 8, indicate that the measurements by alumina crucibles fit in the curve for those by platinum ones.

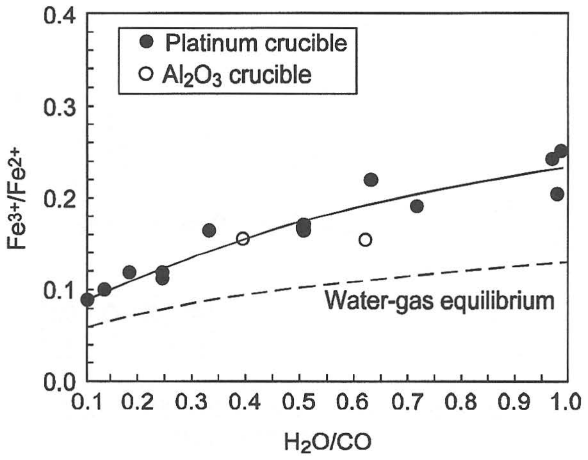

Fig. 8. The steady state Fe^{3+}/Fe^{2+} ratios as a function of H_2O/CO ratio for slag C at 1500°C.

4 DISCUSSION

4.1 Rate equations

When a slag is exposed to H_2O-CO mixtures, the oxygen exchange between the gases and the slag at the interface may be described by the overall reactions[22]:

$$H_2O \Leftrightarrow H_2 + (O) \qquad (2)$$

$$CO + (O) \Leftrightarrow CO_2 \qquad (3)$$

The rate equations appropriate to the steady state measurements for these reactions are readily derived if the order of reaction with respect to the partial pressures of the gas species are known or assumed[3,17]. Considering reaction (3) and assuming that the forward and reverse reactions are first order with respect to the pressures of the gas species, the net rate of the reaction, V_C, may be expressed as

$$V_C = (k_a')_C\, pCO - (k_a)_C\, pCO_2 \qquad (4)$$

where $(k_a')_C$ and $(k_a)_C$ are the apparent first order forward and reverse rate constants for reaction (3). For equilibrium with the surface, Eq.(5) is followed, where K_{eqC} is the appropriate equilibrium constant for reaction (3).

$$\frac{(k_a')_C}{(k_a)_C} = \left(\frac{pCO_2}{pCO}\right)_{eq} = K_{eqC}\, a_o \qquad (5)$$

Combining Eqs.(1) and (5) with (4), Eq.(4) becomes

$$V_C = k_C K_{eqC}\, pCO\, a_o^{1-x} - k_C\, pCO_2\, a_o^{-x} \qquad (6)$$

The apparent rate constant for H_2O dissociation (reaction (2)) is also a function of oxygen activity. The rate of the H_2O reaction with liquid silica-saturated iron silicates has been measured by the isotope exchange technique and the apparent first order rate constant has been found to be inversely proportional to the H_2O/H_2 ratio[16]. For more complex melts, the apparent first order rate constant for H_2O dissociation has been observed to be given by Eq.7 in a study of the dissociation of H_2O over calcium aluminosilicate melts by the isotope exchange technique[28].

$$(k_a)_H = k_H\, a_o^{-y} \qquad (7)$$

Likewise, the general rate equation of reaction (2) is probably as given below,

$$V_H = k_H\, pH_2O\, a_o^{-y} - k_H K_{eqH}\, pH_2\, a_o^{1-y} \qquad (8)$$

where 1). $(k_a)_H$ and $(k'_a)_H$ are the apparent first order forward and inverse rate constants of dissociation of H_2O (reaction (2)); 2). k_H is a system and temperature dependent rate constant for H_2O dissociation; 3). $-y$ is the slope of the plot of $\log(k_a)_H$ against $\log a_o$; 4). K_{eqH} is the equilibrium constant of reaction (2).

Obviously, Eqs. 6 and 8 represent the rates of oxygen removal from and addition to the interface for the oxygen exchange between the CO-H_2O mixture and the melt at the interface. At steady state $V_C = V_H$ and, if the partial pressures of H_2 and CO_2 are negligibly low, we obtain

$$k_C K_{eqC}\, pCO\, a_o^{1-x} = k_H\, pH_2O\, a_o^{-y} \qquad (9)$$

Since oxygen activity is defined as equilibrium CO_2/CO ratio, K_{eqC} is equal to unity, we have Eq.(10) and Eq.(11) holds if x=y.

$$a_o^{1-x+y} = \frac{k_H\, pH_2O}{k_C\, pCO} \qquad (10)$$

$$a_o = \frac{(k_a)_H\, pH_2O}{(k_a)_C\, pCO} \qquad (11)$$

Thus, for a given state of oxidation, the value of the steady state oxygen activity divided by the H_2O/CO ratio gives the ratio of the apparent first order rate constants for the dissociation of H_2O and CO_2.

4.2 Relative rates of reactions of H_2O/H_2 and CO_2/CO

The steady state oxygen activity derived from the measured steady state Fe^{3+}/Fe^{2+} ratio by the appropriate correlation[27] is presented in Fig. 9 as a function of H_2O/CO ratio for slag A at 1350°C. The linear relationship between the steady state oxygen activity and the H_2O/CO ratio may be expressed by Eq.12, where the uncertainty represents one standard deviation.

$$a_o = 5.70(\pm 0.22)\ H_2O/CO \qquad (12)$$

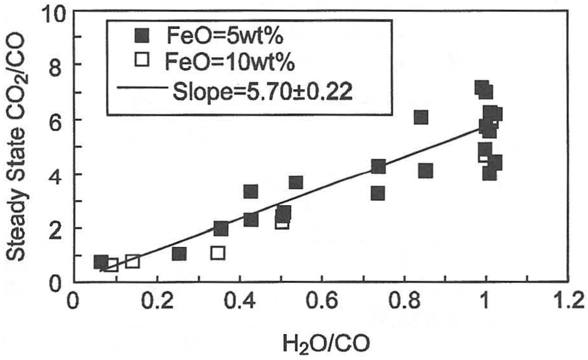

Fig. 9. The steady state oxygen activity as a function of H_2O/CO ratio for slag A at 1350°C.

As shown earlier in Fig. 6, the experimental results for 1300°C could not be distinguished from those at 1350°C. Thus, from Eq.11, the apparent first order rate constant for H_2O dissociation exceeds that for CO_2 dissociation by a factor of about 6 with slag A for iron oxide concentrations in the range of about 5-10 wt% at 1300-1350°C.

4.2.1 Dependence of the steady state values on melt composition

The steady state oxygen activities versus pH_2O/pCO for slags B and C are derived from the steady state Fe^{3+}/Fe^{2+} ratios by the appropriate correlations[27] and presented in Fig. 10. The straight lines drawn through the data are given by Eqs.13 and 14, where the uncertainties refer to one standard deviation.

slag B at 1350-1450°C

$$a_o = 10.43(\pm 0.40)\ H_2O/CO \qquad (13)$$

slag C at 1500°C

$$a_o = 1.88(\pm 0.10)\ H_2O/CO \qquad (14)$$

In reference to the steady state model Eq.11, the apparent first order rate constant for H_2O dissociation is about 10 times that for CO_2 dissociation on slag B, 6 times on slag A and 2 times on slag C. Apparently, a clear trend is followed, ie., the ratio of the apparent rate constants for dissociation of H_2O and CO_2 over these melts decreases with increasing basicity. This ratio is presented in Fig. 11 versus the molar ratio of CaO/SiO_2 of the melts as the measure of basicity. If the Fe^{3+}/Fe^{2+} ratio at a given

pCO_2/pCO ratio or the optical basicity of the melts was to be taken as the measure of the basicity, similar trends would be observed.

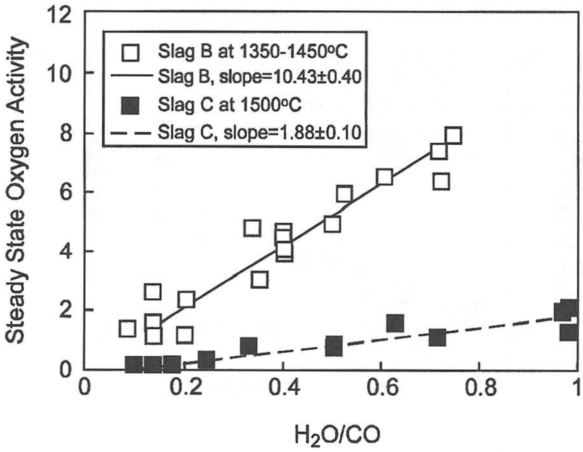

Fig. 10. The steady state oxygen activity as a function of H_2O/CO ratio for slags B and C.

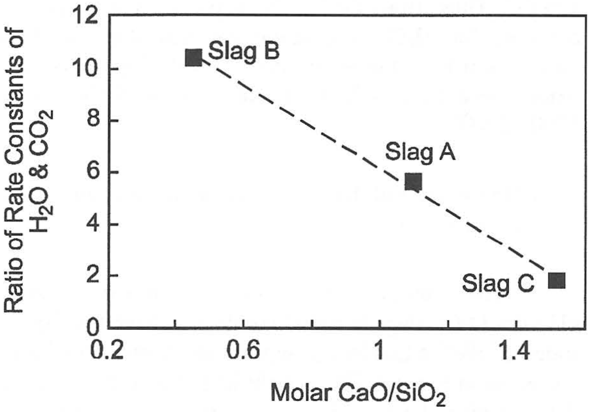

Fig. 11. Ratio of the apparent rate constants of H_2O and CO_2, $\frac{(k_a)_H}{(k_a)_C}$, as a function of molar CaO/SiO_2 ratio of the melts.

4.2.2 Relative rates of H_2O and CO_2 reactions with metallurgical melts

The present study has shown that the apparent rate constant for the H_2O reaction exceeds that for the CO_2 reaction by a factor of up to about one order of magnitude. This is consistent with all existing information for the relative rates on metallurgical melts.

Sasaki and Belton have used the steady state technique to measure the steady state oxygen activity for silica saturated iron silicates under impinging H_2O-CO mixtures at 1250°C[17]. In the range of H_2O/CO ratios of 0.04 to 0.6, the apparent rate constant for dissociation of H_2O was deduced to be about 20 times that for CO_2 over this melt. The oxidation state of liquid lithium silicates containing FeO (0.27 and 1.71wt%), with Li_2O/SiO_2 weight ratio=0.14 and Al_2O_3=7wt%, was also determined at the steady state in flowing H_2-CO_2 mixtures at 1100°C[29]. The rate of dissociation of H_2O was derived to be about 2.1 times that of dissociation of CO_2.

Glaws and Sun have separately measured the dissociation rates of H_2O and CO_2 on CaO-SiO_2-$20Al_2O_3$ melts with CaO/SiO_2=1 and at the very low "FeO" content of 1.0wt% at 1350°C by the isotope exchange technique. This has been reviewed by Belton[28], who showed that the apparent first order rate constant for H_2O dissociation was approximately a factor of 10 times that for CO_2 at the same oxygen partial pressure at 1350°C, which is in good agreement with the present work on slag A.

5. CONCLUSIONS

(1) Steady state, where the rate of oxygen addition by H_2O dissociation matches that of oxygen removal by CO at the gas-melt interface, has been established in melts of the system CaO-SiO_2-Al_2O_3 containing iron oxide under flowing H_2O-CO mixtures.

(2) The steady state Fe^{3+}/Fe^{2+} ratio has been shown to be a function of H_2O/CO ratio only for a given melt. For all melts the steady state Fe^{3+}/Fe^{2+} ratio significantly exceeds the value for water-gas equilibrium.

(3) If the dissociation reactions of H_2O and CO_2 are assumed to be first order with respect to the partial pressures of the gas species, the relative apparent rate constants of reactions of H_2O and CO_2 are given by $\frac{(k_a)_H}{(k_a)_C} = a_o \left(\frac{pH_2O}{pCO}\right)^{-1}$.

(4) The apparent rate constant for the dissociation of H_2O is deduced to be about 6 times that for CO_2 over slag A, approximately 2 times over slag C, and about 10 times with slag B. Thus the ratio of rate constants for H_2O and CO_2 decreases with increasing basicity.

(5) It has been demonstrated that the steady state technique is an effective method to determine the relative rates of reactions of H_2O-H_2 and CO_2-CO over melts. The relative rates of H_2O and CO_2 reactions obtained in this work are of the same order of magnitude as those over metallurgical melts from the previous studies.

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