A comparison of the kinetics of the CO-CO\textsubscript{2} reaction with steelmaking and copper making slags

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Introduction

The reaction between carbon and slags is of significant importance in direct smelting of iron ores, EAF slag foaming and copper slag cleaning processes. This reaction is known to occur via gaseous intermediates and it is important to have fundamental data to understand the relative importance of each reaction step. In this study, the rate of CO\textsubscript{2} dissociation on different slag surfaces is measured using an isotope exchange technique. It was found that increasing iron oxide content up to 30 wt per cent does not have a significant effect on the rate constant while increasing from this limit, increases the rate constant dramatically. Activation energy of CO\textsubscript{2} dissociation on slags of unit basicity and different iron oxide contents is in the range of 180±40 kJ/mol. It is found that rate constant dependence on oxygen potential in the slag phase is increasing with iron oxide concentration. In the case of copper making slags, the influence of copper oxide is found to increase the magnitude of apparent rate constant, while decreasing the activation energy considerably.

Key words: Gas-slag reaction, CO\textsubscript{2} dissociation, copper slag, kinetics, isotope exchange
gas mixture; \( P_{14\text{CO}} \) the partial pressure of tagged CO in the 
reacted gases and \( (P_{14\text{CO}})_{eq} \) is the partial pressure of 
labelled CO if complete equilibrium were to be achieved.

In the present study, the stable isotope \( ^{13}\text{C} \) \( (^{13}\text{CO}_2) \) was 
employed as the tracer isotope. By taking full account of 
the natural abundance of \( ^{13}\text{C} \), Equation [5] was modified as 
follows:

\[
\begin{align*}
\frac{V}{ART} \ln \left[ \frac{1 - P_{13\text{CO}}^i/(P_{13\text{CO}})_{eq}}{1 - P_{13\text{CO}}^i/(P_{13\text{CO}})_{eq}} \right] = k_a
\end{align*}
\]

where all meanings for terms in Equation [5] are valid for 
this equation with the new term \( P_{13\text{CO}} \) being the partial 
pressure of \( ^{13}\text{CO} \) in the inlet gases, i.e. the partial pressure 
of natural \( ^{13}\text{CO} \).

**Experimental procedure**

A slag sample weighting 0.5 to 1 gram was placed in a 
platinum, alumina or zirconia crucible in the vertical 
resistance heated tube furnace. This arrangement is shown 
in Figure 1. Once the desired temperature was achieved, 
CO-CO\(_2\) gas mixture was passed over the slag. Gas 
flowrates were adjusted to yield desired CO\(_2\)/CO ratio and 
flow rate. The overall gas flowrate was kept high enough to 
be in the regime of interfacial chemical control. Each slag 
sample was equilibrated for at least 1 hour under controlled 
CO\(_2\)/CO ratio then labelled gas was introduced. The 
labelled gas contained 10 mol per cent \( ^{13}\text{CO}_2 \), but was 
diluted on mixing. An Isoprime isotope ratio mass 
spectrometer (Micromass) was employed to measure the 
concentration of labelled species in both ingoing and 
outgoing gas samples.

**Results**

**CaO-SiO\(_2\)-FeO\(_x\) Slags**

Experiments were conducted to measure the oxidation rate 
of CaO-SiO\(_2\)-FeO\(_x\) slags with unit basicity \( \text{(CaO/SiO}_2=1.0 \) 
molar) and iron oxide content varying from zero to 90 wt 
per cent. The effect of oxidation state of the slag (fixed by 
the CO\(_2\)/CO ratio and temperature) on the magnitude of rate 
constant was examined for each slag composition.

**Effect of iron oxide content**

Figure 2 shows the dependence of apparent rate constant,

\( k_a \), on the iron oxide content in the slag. A very sharp 
increase in the \( k_a \) is seen with \( \text{'FeO}_x \) content increasing 
above 30 and up to 90 per cent. Data from several other 
studies are included for comparison.

**Effect of oxidation state of the melt**

Dependence of \( k_a \) on the applied CO\(_2\)/CO ratio for some of 
the studied slags is presented in Figure 3. It is seen that log 
\( (k_a) \) decreases linearly with increasing log(CO\(_2\)/CO).

**Effect of temperature**

Figure 4 shows the temperature dependence of \( k_a \) with 
CO\(_2\)/CO=1.0 for slags of unit basicity and different iron 
oxide contents. Activation energy of \( 180 \pm 40 \) kJ/mol is 
obtained for different iron oxide content.

**SiO\(_2\)-Al\(_2\)O\(_3\)-FeO\(_x\)~-\( \text{(Cu}_2\text{O) Slags} \)**

To determine the effect of copper, rate constant 
measurements at varying CO\(_2\)/CO and temperature were
conducted on two slags: copper free slag with 60 wt per cent FeOx, 30 wt per cent SiO2, 10 wt per cent Al2O3 and a slag, with the same wt ratios of FeOx to SiO2 to Al2O3, plus 6 wt per cent Cu2O. The dependence of \( k_a \) on CO2/CO ratio for both slags is provided in Figure 5. An increase in the \( k_a \) is seen while the slope of lines remained essentially constant.

Results of present and previous studies on temperature dependence of \( k_a \) are presented in Figure 6. Addition of copper to slag has lowered the activation energy from 190 to 100 kJ/mol.

**Discussion**

**Rate of oxidation of iron oxide containing slags**

**Effect of oxidation state of the slag**

The relationship between the rate constant of CO-CO2 reaction with slags and the oxidation state of slag can be simply expressed as

\[
k_a = k_a^0 (a_0)^n
\]  

[7]

where \( a_0 \) is the imposed CO2/CO, \( k_a^0 \) is temperature dependent constant for any slag composition and \( n \) characterizes the degree of dependence of rate constant to the oxidation state of the slag.
Variation of $n$ for different iron oxide content is provided in Figure 7. Despite small discrepancies, it is shown that increasing FeO$_x$ from zero to 90 wt per cent, increases $n$ from approximately 0.5 to 1.0.

While many investigators have found an inverse relationship ($k_a = k'_a(a_0)^{-n}$) for the rate of reaction on iron oxide rich or pure iron oxide condense phases, Sun showed that the first order rate constant for CO$_2$ dissociation on CaO-SiO$_2$-Al$_2$O$_3$ slags containing about 1 per cent FeO$_x$ decreased with $a_0$ according to relationship $k_a = k'_a(a_0)^{-0.5}$. El-Rahaiby et al. have also shown that for an equimolar CaO-SiO$_2$-FeO$_x$ slag, $k_a = k'_a(a_0)^{-0.75}$. It is thus apparent that, as FeO$_x$ decreases, $k_a$ dependence on $a_0$ decreases. From results of this study, as seen in Figure 7, it may be concluded that the rate constant dependence on the state of oxidation is variable depending on the total iron oxide content in the slag. Increasing the iron oxide content of the slag, increases the value of $n$ to unity for iron-rich slags.

A mechanism, involving transfer of two negative charges (electrons) to the adsorbed CO$_2$ would lead us to expect a value of 1 for $n$. For a detailed review, the reader is referred to an article by Sasaki et al. Briefly, based on this mechanism, for a given number of reaction sites, the reaction rate is proportional to the surface concentration of weakly adsorbed CO$_2^-$ ions. The ions are formed through following reaction:

$$CO_2^{(ad)} + 2e^- \rightarrow CO_2^{-2}$$

The oxidation state of the slag, affects the electronic defect structure, thereby affecting the electrochemical potential of electrons which finally influence the concentrations of CO$_2^-$. This mechanism explains the value of -1 for $n$. However, it fails to explain the values of $n$ less than 1. There are two possible explanations for the deviation of $n$ from unity in some slag systems, particularly at low iron oxide contents;

Firstly, if adsorbed ions on the slag surface, are produced in the form of singly charged ions (CO$_2$), instead of doubly charged CO$_2$ ions, (CO$_2$)$^-2$, value of $n$, should be 0.5 in ideal slags. This value is very close to low-iron content slags. On the other hand, value of $n$ in the iron-rich end of diagram, is close to 1. Therefore, it can be explained that increasing the iron oxide content of the slag, the dominant mechanism changes from formation of singly charged to doubly charged CO$_2$ ions.

The second probable reason for changing the value of $n$ with FeO$_x$ content may be variation in the electronic structure of slag with variation in iron oxide content. For pure iron oxide, when doubly charged CO$_2$ is adsorbed on the surface, the ‘ideal value’ of $n=1$ is confirmed by this charge transfer model. However, addition of other oxides to the iron oxide can cause variations in its electronic properties thus deviation in the ‘ideal’ behaviour.

**Effect of iron oxide content**

Results of present and some of previous studies have been gathered in Figure 2. An exponential trend is observed in all separate studies. Increasing iron oxide content up to approximately 30 per cent does not have a significant effect on the $k_a$. On the other hand, increasing ‘FeO$_x$’ content, from this limit up to 100 wt per cent increases the rate dramatically. The lower temperature studies of Li et al. and Sun deviate at higher FeO$_x$ contents. This can be attributed to higher temperature in the present study. Assuming a constant activation energy at different iron oxide contents, the observed divergence of the two sets of data is close to the expected. As seen, the agreement with the study of Mori et al. for the experiments conducted at the same temperature as the present work is extremely good.

As noted in previous section, based on charge transfer mechanism, electronic properties of slag can affect the rate of reaction significantly. Several measurements on electrical conductivity of slag show that increasing iron oxide content of the slag, increases the electrical conductivity. Li et al. gathered data on the electrical conductivity of iron oxide melts and showed that electrical conductivity as a function of FeO$_x$ content is analogous to the variations of $k_a$. They concluded that electrical properties of slag are most likely to be the reason for such trend in dependence of $k_a$ on FeO$_x$ content.

**Effect of copper oxide addition**

As shown in Figure 5, addition of 6 wt per cent Cu$_2$O to the slag at 1583K, increases $k_a$ by a factor of 3, while there is no change in the CO$_2$/CO dependency, with a slope of -0.4 for both lines. The effect of copper could be explained in terms of basicity. In general, the apparent rate constant at a given oxygen potential increases with the basicity of the melt. It is reasonable that oxygen transfer is more rapid on a more extensively reduced surface, because of the readiness of CO$_2$ for Cu$^+$ ions in the slag, as described earlier. At this stage, the role of each phenomenon has not been clarified but an investigation of this is ongoing.

The strong influence of copper on the apparent rate constant is also illustrated in Figure 6. This figure shows again that the reduction rate is more rapid on the surface of a copper slag than on that of copper-free slag. The
calculated activation energy is 190 kJ/mole for slag without Cu₂O. However, it is only 100 kJ/mole for slag with Cu₂O.

Results of other studies on similar slags are also shown in Figure 6. The activation energy for copper free slag is very close to El-Rahaiby’s₁₆ result (196 kJ/mol) for a slag with a similar composition. Compared with Uitgard’s₁₈ results, the biggest difference for the rate constants is 1 order within the experimental temperature range after adding Cu₂O. This might be because that there is 0.5 per cent S in Uitgard’s slag.

**Conclusion**

• For CO₂/CO exchange in CaO-SiO₂-FeOₓ-Al₂O₃-(Cu₂O) slags, the rate constant decreases with oxygen potential. This decrease is consistent with a charge transfer mechanism and a rate determining step involving CO₂⁻⁻ formation/dissociation where 0.5 ≤ n ≤ 1.

• The rate constant for a given temperature is represented by the equation

\[ k_n = k \left( \frac{P_{CO}}{P_{CO_2}} \right)^n \]

for an iron silicate slag with and without copper, n=0.4 for CaO-SiO₂-FeOₓ slags, and n is a function of total iron oxide content. For a CuO/SiO₂ slag, n = 0.0048 (%FeO₂)=0.469

• The activation energy was found to be independent of total iron oxide content but was dependent on copper presence in slag. For copper free slags, activation energy was 180kJ/mol. Addition of 6 wt per cent copper oxide, decreased activation energy to 100 kJ/mol.

• For CaO-SiO₂-FeOₓ slags, the rate constant increases significantly with total iron content, when iron oxide increases from approximately 30 wt per cent.

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