Effects of Iron Oxide and Sulphur Content on the Rate of Reduction of ZnO from Slags by CO-CO_2 Gas Mixtures

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ABSTRACT

The kinetics of reduction of a thin layer (5-7 mm) of calcium alumino-silicate slags containing ZnO (3 to 36 wt%) and FeO_x (0.2 to 36 wt%) by flowing CO-CO_2 gas mixtures were studied at 1300 °C under conditions where mass transfer was not limiting the reduction rate. The results obtained show virtually no dependence on the ZnO concentration over the range studied, but show a strong dependence of the rate on the iron oxide content of the slag. The measured rates were mildly affected by the sulphur content of the melts, but increased significantly with addition of 2 wt% Na_2O to the slag. Analysis of these data suggests that the kinetics of adsorption/desorption species at the gas-slag interface does not control the kinetics of reactions at the interface. The deduced first order rate constant for the iron oxide rich slags is in accord with the isotope exchange data for the rate of formation of CO_2 on the surface of melts with comparable chemistry and temperature. These findings indicate that presence of ZnO in iron rich slags does not significantly influence the rate of formation/dissociation of CO_2 at the interface.

1. INTRODUCTION

The direct bath smelting processes developed for production of non-ferrous metals share two important features; namely, well mixed high intensity reactors and the use of coal for fuel and reductant. The production of lead and zinc by such processes involves oxidation of sulphide ores to form a slag phase followed by reduction of the slag with carbonaceous materials. While the thermodynamics of zinc containing slags has been researched to the extent that the chemical driving force for reduction and fuming of zinc from simple and complex slags can be estimated, the existing knowledge on the kinetics of reactions between zinc slags and gaseous reactants such as CO, CO_2, H_2 and H_2O is far more scarce and too incoherent to be used for answering questions such as how fast these new smelting processes can be driven and/or to what extend one can improve the coal utilisation rate.

Over the past decade, the knowledge of the transport properties of simple zinc free slags and the interfacial rates of reactions between such slags and CO-CO_2 gas mixtures has progressed to the point where greater emphasis is being placed on the rates of interfacially controlled chemical reactions in highly intensified smelting processes.

Recent studies on the kinetics of interfacially controlled reactions between CO-CO_2 gases and ferrous and non-ferrous slags containing iron oxide have shown that, apart from the concentration of iron oxide, the oxidation state of the slags can have a strong effect on the reduction and oxidation rates[2-5]. Through the work of Belton and his co-workers, these effects have been attributed to the ease of charge transfer between adsorbed species such as CO_2^{2-} and the Fe^{3+}-Fe^{2+} redox reactions[2-3]:

$$CO_2^{2-} + 2\,Fe^{3+} = 2\,Fe^{2+} + CO_2 \qquad .. [1]$$

Most metallurgical slags produced through use of coal for smelting and reduction contain up to 3 wt% sulphur. The apparent retarding effect of sulphur on the zinc fuming rates in industrial reactors has been noted by a number of investigators and reported by Grant[6]. Sulphur, which is surface active in metals[7] and slags[8], could influence the rates of interfacial reactions through the adsorption/desorption kinetics as well as through the interfacial area between reaction phases. The action of surface active agents such as sulphur in reducing the number of vacant sites on the surface of liquid iron alloys for CO-CO_2 reaction, has now been well established[9]. However, results by Kim, Graenzoerffer and Fine[10] on the effect of sulphur on the kinetics of CO-CO_2 reaction with slags show some interesting, but inconclusive behaviour. Their data show an initial slowing of the rates by about 20%, when the sulphur content in the slag is less than 0.1 wt%, and a three fold increase in the rates as the sulphur content was raised beyond 0.1% to about 1 wt%.

Oxides of phosphorus and sodium in slags also cause lowering of surface tension of the melts and kinetic studies have shown that, while the addition of P_2O_5 lowers the apparent first order rate constant for reduction/oxidation of iron oxide containing melts by CO-CO_2, additions of Na_2O increase the reaction rate contant[13,14]. These opposing effects of P_2O_5 and Na_2O in simple iron oxide containing melts has been reviewed by Sun and Belton and explained in terms of their effects on changing the surface basicity and hence the Fe^{3+}/Fe^{2+} ratio at the gas-slag interface[14,15].

In terms of kinetic studies on zinc slags, there has been a number of investigations carried out under conditions where the interfacial reaction area were not controlled and where the measured rates are possibly in a mixed controlled regime[16-18]. Van Germert *et al.*[17] and Rankin and Wright[18] have shown that the presence of iron oxide in the slag results in increasing the reduction rate. While the effects of iron oxide content and its oxidation state on the interfacial rate of reduction of lead slags (in the presence and absence of zinc oxide) have been studied and partially reported[5], there is still lack of kinetic data on the interfacial reactions between CO-CO_2 and lead free slags of interest in zinc fuming processes. The present work was aimed at determining the effects of iron oxide and surface active agents, such as S and Na_2O, on the reduction kinetics of zinc slags by CO-CO_2 gas mixtures, under conditions where the rates are not influenced by mass transfer in the slag and gas phase.

2. EXPERIMENTAL

Master slags were prepared by mixing appropriate amounts of high purity (>99.5%) Al_2O_3, $CaCO_3$, SiO_2, Fe_2O_3 and metallic iron powder and pre-melting the mixture in alumina crucibles at 1300 °C. A number of master slags with CaO/SiO_2 ratios in the range 0.65 to 0.8 and different FeO_x content were prepared; the composition of these slags are shown in Table I. In some experiments, FeS or Na_2O was used for doping the master slags with S or Na_2O, respectively. In experiments where an intermediate sulphur content (between 0 and 2.5%) was required, an appropriate mixture of low and high sulphur content slags were used.

Table I: Composition of the initial slags (in wt %) used.

Slag	CaO	Al_2O_3	SiO_2	FeO	Fe_2O_3	S	ZnO
1	25.58	8.05	31.21	<0.20	-	0.00	35.6
2	33.12	9.63	43.46	13.01	0.80	0.00	12 - 15
3	28.17	11.83	35.26	22.29	2.45	0.00	12 - 15
4	18.79	11.25	27.68	29.45	2.20	0.00	12 - 15
5	19.57	14.45	27.96	34.71	0.77	0.00	12 - 15
6	17.82	4.52	26.79	25.21	11.38	0.00	14.25
7	17.12	4.35	26.58	26.36	8.83	2.50	14.26

For each experiment the required amount of ZnO was weighed and well mixed with about 5 g of the master slag. The mixture was then placed in an alumina crucible (20 mm OD, 16 mm ID and 30 mm height). The CO, CO_2 and Ar were dried and purified using the standard techniques. A pre-calibrated mass flow controller was used for preparing the CO-CO_2 gas mixture.

The basic apparatus used for the kinetic studies is shown in Figure 1. The experiments were carried out in a vertical tube furnace heated with silicon carbide elements and controlled to within 5 °C of the required temperature by a PID controller. Temperature measurements were made with a Pt/Pt-13%Rh thermocouple located at the base of the recrystallised alumina crucible. The atmosphere inside the Pythagoras work tube (50 mm ID) was isolated by gas tight water cooled brass fittings. The gas exist was through bubblers.

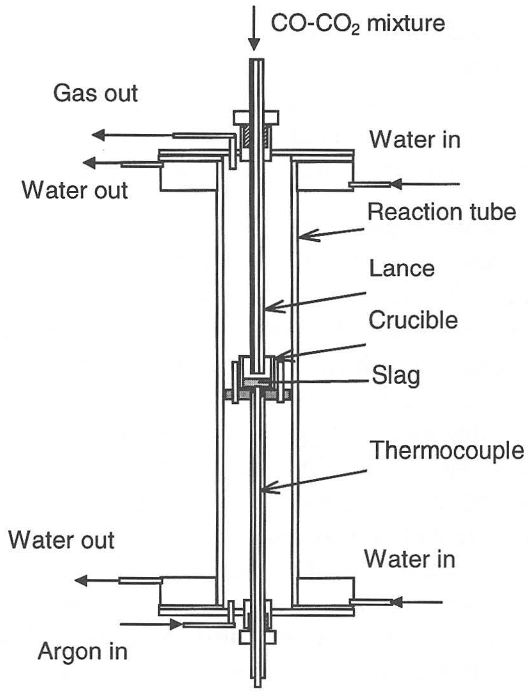

Figure 1: Experimental apparatus.

In each experiment, after flushing the furnace atmosphere with nitrogen or argon, the crucible containing the slag was placed in the hot zone of the tube furnace and heated to the required temperature under an atmosphere of argon at a rate of 6 °C/min The slag was then allowed to homogenise for 30 minutes before exposing it to a flowing CO-CO$_2$ gas mixture. The stream CO-CO$_2$ mixture was blown on to the surface of the melt through an alumina tube (8 mm OD, 5 mm ID). The distance between the tip of the tube and the surface of the melt was about 13 mm. In some experiments an alumina rod (about 3 mm OD) was attached to the end of the tube for mechanical stirring of the melts. In these experiments, the effect of rotation speed (0 to 200 rpm) of the rod on the reduction rates of melts was studied at 1300 °C.

At the end of the required reduction period with CO-CO$_2$, the crucible was lowered to the lower brass fitting where it was cooled by a stream of nitrogen. The time taken to cool the crucible and its content to temperatures below the solidus was less than one minute. After separating of the slag from the crucible material, the slag was ground and then analysed for major components (Al, Ca, Fe, Si and Zn) by x-ray fluorescence (XRF) or using an Inductively Coupled Plasma and for S by the XRF or Leco analyser. The ferrous oxide concentration and total iron were determined by titrating dissolved samples with $K_2Cr_2O_7$.

3. RESULTS AND DISCUSSION

Typical results obtained by reducing about 5 g of the high zinc slag at 1300 °C by CO-48%CO$_2$ gas mixture flowing at about 0.95 l/min are shown in Figure 2. The results show reduction of ZnO and increase in FeO contents as the reduction proceeded. The changes in the Fe_2O_3 and CaO concentrations with reduction period appear to be small. It is worth noting that while the reduction of Fe_2O_3 to FeO took place at a relatively slow rate, the decrease in the mass of slag resulting from reduction of ZnO resulted in the concentration of Fe_2O_3 to appear appears nearly constant in these runs. The Al_2O_3 content of slags increased by about 4 to 5 wt% over the 90 min.

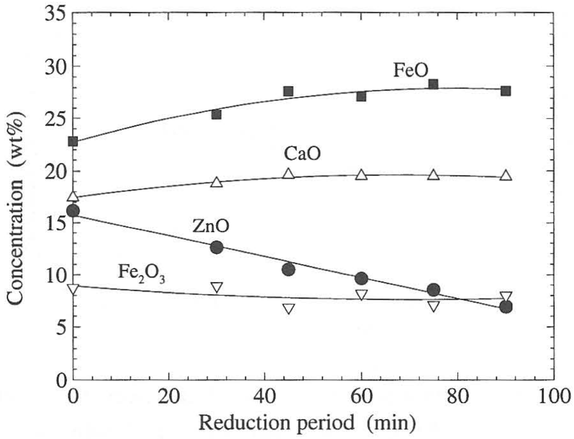

Figure 2: Typical results obtained from reduction of zinc slags with CaO/SiO$_2$ of 0.76 by CO-48% CO$_2$ at 1300 °C.

The results shown in Figure 2 also show that the reduction rate of ZnO (R_{ZnO}) was not affected by the concentration of ZnO in the slag. Similar behaviour was observed when slags with higher initial ZnO contents were reduced to about 3 wt% ZnO.

3.1 Mass Transfer in the Gas Phase

A number of experiments were carried out to establish the conditions under which the reduction rates were predominately independent of mass transfer in the gas phase. The total rates ($R_{tot} = R_{ZnO} + R_{Fe2O3}$) are plotted against the flow rate of $CO\text{-}CO_2$ gas mixture in Figure 3. At low gas flow rates there was an apparent dependence of the specific reduction rate on the reductive gas flow rate. However, at flow rates in excess of 0.8 l/min the reduction rates became independent of the flow rate.

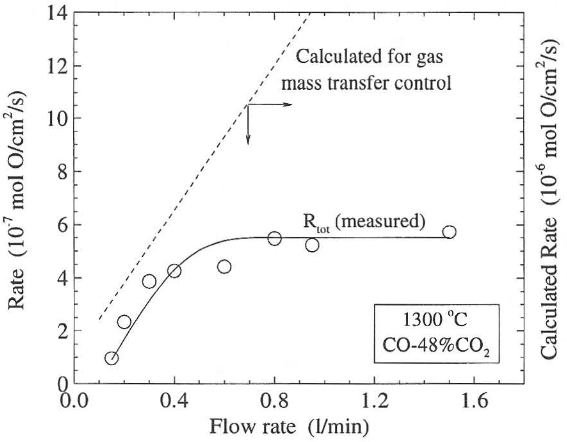

Figure 3: Dependence of the reduction rates at 1300 °C on the flow rate of CO-48%CO_2 mixture. The calculated curve for gas phase mass transfer control is based on the correlation by Saito *et al*[20]

In Figure 3, the calculated rates for the gaseous mass transport control are also shown. These rates were calculated from the correlation proposed by Saito *et al.*[19] and the physical properties of the gaseous phase in the boundary layer adjacent to the slag-gas interface. It was assumed that the activity of ZnO in the slag was about 0.2 and hence the equilibrium partial pressure of CO at the slag-gas interface was about 0.45 atm. Comparison of the calculated rates with the total reduction rates deduced from the experimental data shows that the measured rates are considerably slower than the calculated rates and, hence, measured rates are unlikely to be controlled by mass transfer in the gas phase.

With respect to the effect of gas flow rate on the partial pressure of zinc in the gas phase and, hence, its removal rate from the slags, the experimental results show only a slight increase in the apparent reduction rate in the plateau region. This apparent increase is well within the uncertainties and suggests that the measured rates could only be mildly dependent on the rate of removal of zinc vapour from the interface; i.e, the rate of reduction was much slower than the rate of mass transfer in the gas phase. This was confirmed through a series of experiments in which N_2 and Ar were substituted for CO and CO_2. It was decided to use a flow rate of about 0.95 l/min for all subsequent experiments.

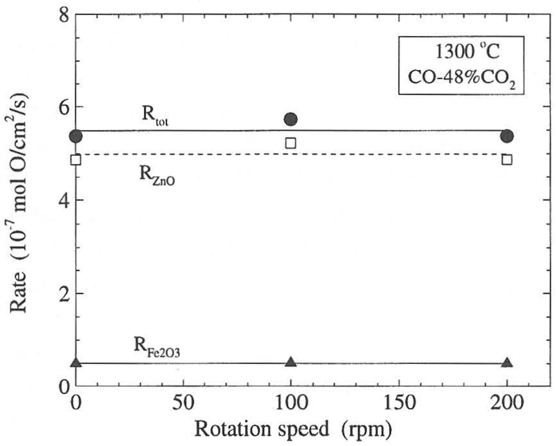

Figure 4. Effect of stirring rate of the slag on the reduction rates of Fe_2O_3 (R_{Fe2O3}), ZnO (R_{ZnO}) and total oxygen ($R_{tot} = R_{ZnO} + R_{Fe2O3}$) at 1300 °C by $CO\text{-}CO_2$.

3.2 Mass Transfer in the Slag Phase

Experiments were carried out to examine the effect of mechanical stirring of the slags on the reduction rate by $CO\text{-}CO_2$ gas mixture. The results are plotted in Figure 4 and show that the reduction rates of ZnO and Fe_2O_3 are not affected by the stirring rate at CO/CO_2 ratio of about 1.1. This finding is consistent with previous work[5] on lead and zinc containing slags in which the reduction rates were found to be independent of mechanical stirring, as well as the thickness of the liquid slags, when the melt depth was less than 10 mm. Furthermore, recent study by Sayad-Yaghoubi *et al.*[20] on the chemical diffusion of oxygen in iron rich slags has revealed that the inter-diffusivity in such slags is of the order of 10^{-3} cm^2/s at 1605 °C with an activation energy of less than 20 kcal/mol. Accordingly, the expected diffusion coefficient at 1300 °C would be about 10^{-3} cm^2/s. Using this value of diffusivity in conjunction with the measured rates of oxygen removal (~$5x10^{-7}$ $mol/cm^2/s$) from the present study, it can be shown that for stagnant melts of less than 10 mm in depth, the kinetics are most unlikely to be controlled by diffusion/mass transfer in the slag phase.

Additional evidence which further supports the above conclusion came from experiments that the reductant type was changed to either metallic iron or H_2 containing gas mixtures[21,22]. The results showed a considerable increase in the reduction rate of zinc slags. It is thus reasonable to conclude that under the experimental conditions employed, the reduction rates of slags by $CO-CO_2$ gas mixtures were not controlled by mass transfer in the slag phase.

3.3 Effects of Sulphur and Soda Additions

In experiments aimed at quantifying the effects of sulphur or soda additions to the slag, some loss of sulphur and soda occurred during the homogenisation and reduction periods. The degree of loss depended on the initial concentration of these additives and increased with increasing initial content. When the slag contained more than 2 wt% sulphur, it could not be retained in the crucible for the length of the experiments and a significant portion of the slag was observed to creep up the walls of the alumina crucible and caused an apparent overflow effect. This indicates that sulphur had a considerable effect on the interfacial tension between the slag and alumina. It is interesting to note that while soda is also expected to be surface active in silicate slags, the overflowing behaviour was not observed to the same extent when soda was added to these slags. Figure 5 shows the dependence of reduction rates (R_{tot}) on the sulphur content of slags which had an initial total iron content of 29 wt%. It is evident that the reduction rates increased slightly with increasing sulphur content. In view of the observed effect of sulphur on the surface tension of these slags, this apparent rise in the reduction rate is likely to be due to the effect of sulphur on increasing the interfacial area for gas-slag reaction. Such a mechanism may be also responsible for the three fold increase in the reduction rates of slags observed by Kim *et al.*[10].

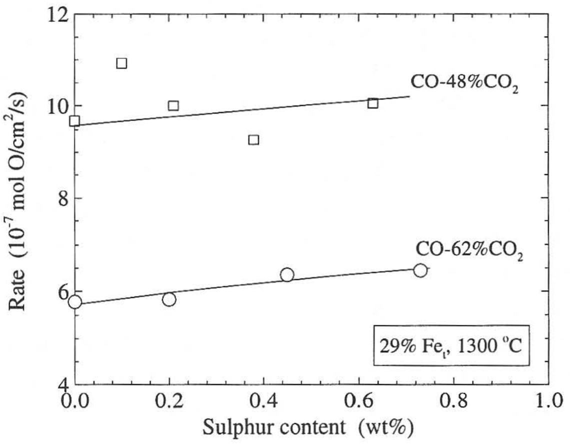

Figure 5. Effect of mean sulphur content on the rates of reduction of zinc slags containing about 29% total Fe by $CO-CO_2$ gas mixtures.

With respect to the effect of soda on the reduction rates, the results show that addition of about 2 wt% Na_2O resulted in increases in the reduction rates of ZnO and Fe_2O_3, from $7.6x10^{-7}$ and $2.1x10^{-7}$ to about $9x10^{-7}$ and $2.4x10^{-7}$ $mol/cm^2/s$, respectively, at 1300 °C. Given that the addition of 2% soda did not increase the wetting between the slag and alumina crucible to a significant extent, then it is likely that the effect of soda on the reduction rate could be due to increasing the surface basicity of the slag and, hence, enhancing the interfacial rate of reaction between $CO-CO_2$ and the $Fe^{3+}-Fe^{2+}$ through reaction [1]. It follows that the role of adsorption/desorption kinetics in reduction of slags by $CO-CO_2$ could be insignificant. In another words, the rates of other reactions at the interface are sufficiently slow that the fraction of sites available for adsorption/desorption does not affect the overall kinetics. This deduction is in accord with analyses of data on $Al_2O_3(sat)-CaO-$

FeO_x-SiO_2 melts[23] and other iron oxide rich melts[14, 15].

3.4 Effect of Iron Oxide Content

A number of runs were carried out to examine the effect of iron oxide content (0.2 to 36 wt % FeO_x) of the slags on the reduction rate. The results are presented in Figure 6 which shows that, although reduction of zinc oxide from the low iron oxide slags occurred rapidly, addition of iron oxide enhanced the rate. The effect of iron oxide became more pronounced at iron oxide contents of greater than 15 wt%. The presence of iron oxide increases the diffusivity of oxygen in slags[20], thus it might be argued that the observed effect of iron oxide on the reduction rate could be due to its effect on inter-diffusivity in these slags. While it is possible that at very low concentrations of iron oxide the effect of diffusion in the slag could become more significant, it has been shown by Sun[14] and Tran *et al.*[24] that the rate of formation and dissociation of CO_2 at the gas-slag interface is dependent on the iron oxide content of slags.

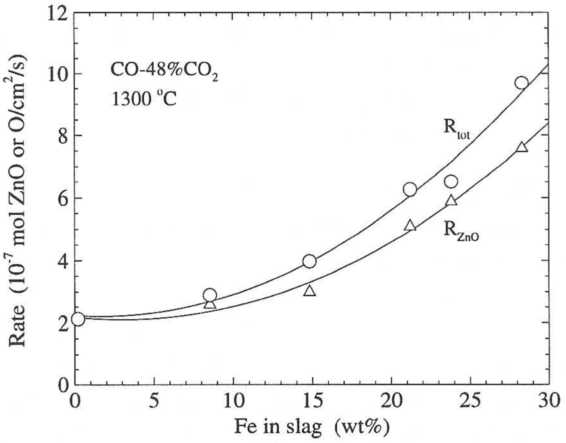

Figure 6. Effect of iron oxide content of slags on the reduction rate by CO-CO_2.

The observed dependence of the reduction rate of ZnO with iron oxide content of the slag indicates that there is a good coupling within the redox reaction:

$$(ZnO) + 2(FeO) = (Fe_2O_3) + Zn(g) \quad .. [2]$$

In lead and zinc containing slags a similar observation has been made under conditions where mass transfer in the gas or slag phase was not the rate determining step[5]. In that study, the measured rates were used to determine the apparent first order rate constant for the rate of formation of CO_2 at the interface. At high oxidation states of the slag, or high oxygen activity, the apparent rate constant showed strong dependence on the oxygen activity as well as on the iron oxide content of the slags. At lower oxygen activity in the melts, where PbO and ZnO are unstable, the rate constants were in good agreement with the isotope exchange data for the rate of formation of CO_2 on surfaces of slags with similar compositions. The results from the present work were treated in a similar manner for the reaction:

$$CO(g) + (O) = CO_2(g) \quad .. [3]$$

for which the reduction rate (R_{tot}) can be expressed as:

$$R_{tot} = k_{app}\ (p_{CO} - p_{CO}^{e}) \quad .. [4]$$

$$\text{or} \quad R_{tot} = k_{app}\ (p_{CO} - p_{CO2}/a_O) \quad .. [5]$$

In Eqns. [4] and [5], k_{app} is the apprent first oder rate constant (which is system and temperature dependent), p_{CO} and p_{CO2} are partial pressures of CO and CO_2 in the gas phase, p_{CO}^{e} is the partial pressure of CO in equilibrium with the slag, k_{app} is the system and temperature dependent apparent rate constant and a_O is the oxygen activity of the slag (not activity of oxygen ions O^{2-}) with respect to unit CO_2/CO ratio as standard state. The values of a_O were estimated through application of a regular solution model to the slag composition[26].

Figure 7 shows the variation of the apparent rate constant with the oxygen activity of the slags. It is evident that while the concentration of iron oxide has a marked effect on the rate constant, the oxidation state of the slags expressed as oxygen activity has no significant effect. Belton and co-worker[2,3,23] studied the kinetics of dissociation of CO_2 on the surface of various iron oxide containing slags. Their findings on the inverse dependence of the first order rate constant (for oxidation of slags by CO-CO_2) on the oxygen activity of the melts were attributed to the need for transfer of two electrons to the adsorbed CO_2 molecules. They concluded that the rate of dissociation of CO_2 on the surface of such slags is dependent on the ease of charge transfer between the adsorbed activated complex (CO_2^{2-}) and slag. For the reduction by CO, the reverse reaction could apply and reaction [1] could be represented by:

$$CO_{(ads)} + (O^{2-}) = CO_2^{2-}{}_{(ads)} \quad .. [6]$$

$$CO_2^{2-}{}_{(ads)} + 2(Fe^{3+}) = 2(Fe^{2+}) + CO_{2(ads)} \quad .. [7]$$

It follows that if the same mechanism is also responsible for controlling the reduction of ZnO containing slags by CO-CO_2, then the rate constant should be dependent on the ability to transfer electrons between adsorbing species at the slag-gas interface. Given that the electrical conductivity of slags is strongly dependent on their iron oxide content[25,26], then the observed dependence of the rate and apparent rate constant on the iron oxide content of slags is an indication of the similar mechanism operating.

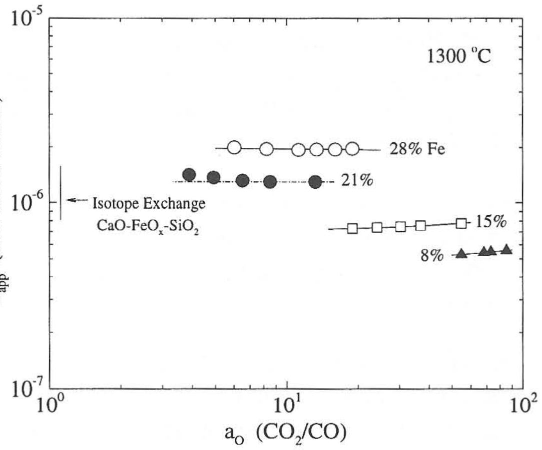

Figure 7. Variation of the apparent first order rate constant (k_{app}) with oxygen activity of slags (a_O) at 1300 °C for slags with different iron oxide content.

Also shown in Figure 7 are the values of apparent constants deduced from isotope exchange studies on calcium iron silicate slags at temperatures close to 1300 °C[23]. It is interesting to note that extrapolation of the present results to low oxygen activity in the slag (i.e. low ZnO contents) gives values which are in broad agreement with the isotope exchange data. The weak dependence of k_{app} on the zinc content of the slags indicates that unlike basic oxides such as CaO, PbO and Na_2O, ZnO does not effect the Fe^{3+}/Fe^{2+} ratio in the slag or at the interface and hence does not make significant contribution toward ease of charge transfer between the adsorbed species at the interface.

CONCLUSIONS

Rate data on the kinetics of reactions between ZnO containing slags and CO-CO_2 gas mixtures were obtained under conditions where mass transfer steps did not influence the kinetics. The measured rates were not affected by the ZnO content of the slags over the range (3-36 wt%) studied, but increased considerably as the iron oxide content of the slag was increased from 0.2 to 36 wt%.

Additions of surface active agents (S and Na_2O) to the iron rich slag did not reduce the rate and tended to increase the reduction rates by CO-CO_2. This behaviour suggests that the rates of adsorption/desorption of species at the slag-gas interface were not limiting the reduction rates and that the rate was controlled by other interfacial reactions, such as the rate of formation of CO_2 at the interface.

The deduced first order rate constant for iron oxide rich slags are in accord with the isotope exchange data on the rate of dissociation and, hence, formation of CO_2 on the surface of melts with comparable chemistry and temperature. The effect of ZnO content of the slag on the apparent first order rate constant is negligibly small.

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