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STUDIES ON THE REDUCTION KINETICS OF METALLURGICAL LEAD SLAGS

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SYNOPSIS

Measurements of the rates of reduction of high lead ISASMELT slag (Al_2O_3-CaO-FeO_x-MgO-PbO-SiO_2-ZnO) by blowing a CO-CO_2 gas mixture on a thin layer of slag (3-10 mm) were made at temperatures in the range of 1180-1320°C. These experiments were carried out under conditions where mass transfer in the gas or slag phase was not the rate controlling step. The experimental findings indicate that the rate of formation of CO_2 at the gas/slag interface is most likely to be the rate controlling step under the above conditions. The dependence of the apparent rate constant on the slag chemistry is discussed in terms of the rate controlling mechanism.

KEY WORDS: ISASMELT, slags, reduction, lead oxide, gas-slag reactions, interfacial kinetics.

INTRODUCTION

The published studies on the reduction or oxidation kinetics of lead slags are limited and deal mainly with binary or ternary iron free lead silicate melts[1-5]. Most of these studies were aimed at illustrating factors which have marked influence on the electrochemical transport of oxygen in lead silicates. Given that the presence of transition metals in metallurgical slags will promote electronic conductivity and there is lack of information and understanding of the behaviour of iron containing lead slags. The work carried out at CSIRO was mainly directed towards the development of an understanding of the mechanism and rate controlling steps in reduction of lead and zinc from ISASMELT and some synthetic slags. Whenever possible the experimental studies were carried out over a broad range of temperature, slag and gas compositions, so as to quantify the effects of these variables on the kinetics of reactions. Use was also made of different experimental techniques to simulate two extreme conditions with respect to mixing/mass transfer in the slag phase.

EXPERIMENTAL DETAILS

The basic experimental arrangement used for studying the reduction kinetics of high lead slags with a CO-CO_2 mixture or metallic iron is shown in Figure 1. The experiments were carried out in a vertical tube furnace heated with six silicon carbide heating elements, controlled to $\pm$ 2 °C. Temperature measurements were made with a Pt/Pt-13%Rh thermocouple located at the base of the recrystallized magnesia crucible, which was about 30 mm high with internal diameter of 16mm. The atmosphere inside the Pythagoras work tube (~50 mm I.D.) was isolated by gas tight water-cooled brass fittings and the gas exit was through bubblers.

The CO-CO_2 mixture used for some of the reduction studies was blended, using pre-calibrated mass flow controllers, then mixed and dried in a column of silica gel. In experiments where H_2-H_2O-Ar or H_2-H_2O-He mixtures were used instead of CO-CO_2, a double water saturater[6] was used in conjuction with the mass flow controllers.

Slags were prepared by mixing appropriate amounts of ISASMELT high lead granulated slags (1.28 ± 0.32 %Al_2O_3, 2.28 ± 1.51 %CaO, 0.29 %Cu, 13.6 ± 0.2 %Fe_t, 0.45 ± 0.05 %MgO, 0.05 %MnO, 51.7 ± 0.1 %Pb, 0.23 %S, 8.4 ± 0.6 %SiO_2 and 8.2 ± 0.6 %Zn) with high purity calcium carbonate. In some experiments use was made of pre-reduced ISASMELT slag containing about 10% PbO. For synthetic slags high purity materials were mixed, calcined and pre-melted in a noble metal or recrystallized magnesia crucible then quenched and pulverised.

The furnace atmosphere was flushed with nitrogen and the magnesia crucible containing 5-10 g of slag was raised to the hot zone of the furnace. The temperature was then increased from 800 °C to the required temperature and the slag was allowed to homogenize for about one hour under an atmosphere of dried nitrogen, flowing at 0.5 $l.min^{-1}$ (STP). Following homogenisation, the slag was reacted with either a stream of gas mixture (CO-CO_2 or H_2-H_2O) or an iron rod, at a similar temperature to the slag, for the required period.

In experiments where $CO-CO_2$ was used as reductant, the gas mixture flowing at about 0.85 to 1.0 $l.min^{-1}$ (STP) was blown on the surface of the melt through a 5 mm I.D. alumina tube, which was about 13 mm above the slag surface. After the required reaction period the crucible was quickly withdrawn from the hot zone of the furnace and quenched in the water-cooled section of the brass end cap under an atmosphere of flowing nitrogen. In some of these experiments the melts were stirred by a magnesia rod attached to a rotating alumina lance. When melts were stirred, the reducing gas ($CO-CO_2$) flowing at about 0.85 $l.min^{-1}$ was blown on the surface of the melt through the rotating alumina lance.

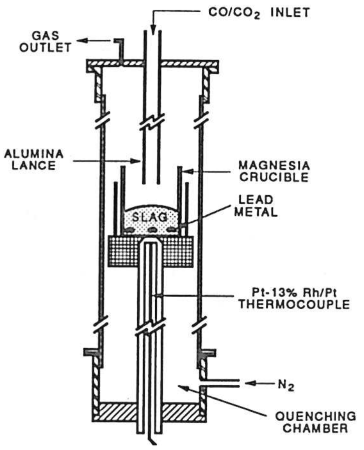

Figure 1: Experimental arrangement used for small scale kinetic studies.

In other experiments where metallic iron was used as reductant, the recrystallized alumina lance was replaced with a clean iron rod (8 mm O.D.) and allowed to heat up to the experimental temperature during the homogenization period. The iron rod was then immersed into the slag bath until it touched the bottom of the crucible containing 10 g of slag. After the reaction period, the iron rod was raised and the crucible was quickly withdrawn from the hot zone of the furnace and placed in the quenching chamber.

After careful separation of the slag from the crucible material, the slag samples were lightly pulverized in a tungsten carbide ring mill for a short period (5-10 s) then passed through an 80 micron sieve. This procedure ensured that over 80% of the metallic lead content of slags (typically 1-2 wt.%) was separated from the slag phase. The slag samples were then analysed for major oxides by Inductively Coupled Plasma (ICP) technique. The ferrous oxide and in some cases metallic lead contents of the samples were determined by standard titration techniques. The estimated accuracy (2 S.D.) of the analyses are about ±2% of the determined values by the ICP and about ±0.5 wt.% and ±0.2 wt.% for the ferrous and metallic lead contents of samples.

RESULTS AND DISCUSSIONS

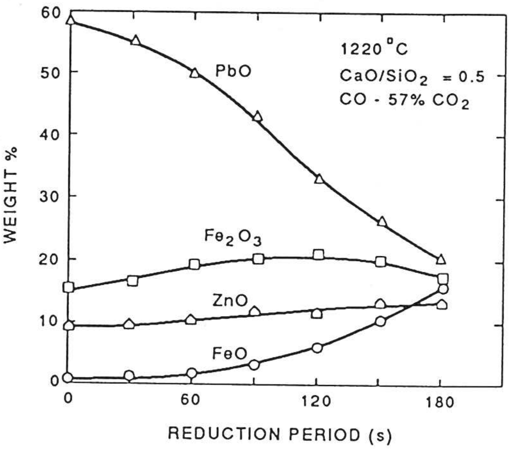

Figure 2: Typical results obtained from reduction of fluxed ISASMELT slag with $CaO:SiO_2 \sim 0.5$, by CO-57% CO_2 at about 1220 °C.

Typical results obtained from reduction of about 5 g of fluxed high lead ISASMELT slag by a $CO-CO_2$ gas mixture are shown in Figure 2. The results show initial high rates of PbO (R_{PbO}) reduction accompanied by the reduction of Fe_2O_3 to FeO. In these zinc containing slags, as reduction proceeds the reduction rate of PbO decreases and the concentrations of total iron and zinc oxide in the slag increases. Reduction of zinc from the slags commenced at a relatively low PbO content.

Initially a number of experiments were carried out to establish the conditions under which reduction rates were predominantly independent of mass transfer in the gas phase. In Figure 3 the measured specific total reduction rate ($R_{tot} = R_{PbO} + R_{Fe2O3} + R_{ZnO}$) for slags containing about 45 and 33 wt% PbO are plotted against the flow rate of the $CO-CO_2$ gas mixture at STP. At low gas flow rates there is an apparent dependence of the specific reduction rate on the reductive gas flow rate. However, at higher flow rates the reduction rate was virtually independent of gas flow rate. In this Figure the calculated rates for the gaseous mass transport controlled regime are also included. These calculated rates are based on the correlation proposed by Saito *et al.* [7]. Comparison of these results show that at gas flow rates of greater than 0.5 $l.min^{-1}$ the total reduction rate could not be affected by the transport of species in the gaseous boundary layer adjacent to the melt surface. It was decided to use flow rates in the range of 0.83 to 1.0 $l.min^{-1}$ (STP) in all the subsequent studies using $CO-CO_2$ gas mixtures.

A similar approach was used for studying the dependence of reduction rate on the flow rates of Ar-25%H_2-6%H_2O and He-25%H_2-6%H_2O. These results showed that a total gas flow rate of about 2 $l.min^{-1}$ (STP) was necessary to overcome the gas mass transfer controlled regime for low lead ISASMELT slags at 1320 °C.

Mass Transfer in the Slag Phase

Results from two series of experiments in which the depth of the virtually stagnant melt was doubled showed that neither the total specific reduction rate (R_{tot}) nor the specific PbO reduction rate (R_{PbO}) were affected by the melt depth. Results obtained from another series of experiments in which the slag was stirred by a magnesia rod (attached to a rotating alumina lance) are shown in Figure 4. It is evident that mechanical stirring of the melts has no significant effect on the measured reduction rates.

Other evidence obtained also negates transport in the slag phase as being the rate controlling step in reduction of lead slags by carbonauous reductants. The best example is the dependence of reduction rate on the reductant type. When hydrogen was used under similar conditions the reduction rate was considerably faster, see Figure 5.

Based on the evidence presented above, it is reasonable to conclude that, at least up to the reduction rates of 5x10^{-5} moles cm^{-2} s^{-1}, transport in the slag phase is unlikely to be the rate controlling step when carbonaceous reductants are used for reduction of lead slags at 1220°C.

Interfacial Chemical Reactions at the Gas-Slag Interface

In Figure 6 the dependence of the total reduction rate on the calculated oxygen potential of slag is shown. In cases where CO-CO$_2$ gas mixtures were used, the rate is proportional to the partial pressure of CO (p_{CO}). Since these results were obtained under conditions where mass transfer limitation in the gas phase was overcome, then the overall reduction rate could be controlled by;

- adsorption/desorption phenomena at the gas-slag interface,

and/or
- chemical kinetics (rate of formation of CO$_2$ at the gas-slag interface).

On considering the overall reaction at the gas-slag interface as:

$$CO\,(g) + (O)_{slag} = CO_2\,(g) \qquad \text{... (1)}$$

then this overall reaction (1) could consist of several intermediate steps such as adsorption of CO:

$$CO\,(g) + \text{vacant site} = CO_{(ads)} \qquad \text{... (2)}$$

the chemical reaction between the CO$_{(ads)}$ and oxygen in the slag phase;

$$CO_{(ads)} + (O)_{slag} = CO_{2(ads)} \qquad \text{... (3)}$$

and desorption of the adsorbed CO$_2$ (CO$_{2(ads)}$);

$$CO_{2(ads)} = CO_2\,(g) + \text{vacant site} \qquad \text{... (4)}$$

If for example the rates of reactions (3) and (4) are sufficiently fast, so that the rate of adsorption of CO becomes limited by the number of vacant sites available for the colliding CO molecules to fill, then the overall rate will be determined by the rate of adsorption of CO.

In a number of Figures presented above, the apparent dependence of the total reduction rates of ISASMELT slag on the a_{PbO} were shown. Since the a_{PbO} decreases as the activity of silica (a_{SiO2}) increases, and silica is found to be a surface active oxide in most slags[9], then it is possible that the decrease in the reduction rates of these slags as aPbO decreases was due to the increase in the a_{SiO2} and hence coverage of the vacant sites by surface active silicate ions. This would be consistent with the explanations offered by Pal *et al.*[2, 3] for their results on the effect of P$_2$O$_5$ on reduction of PbO-SiO$_2$-P$_2$O$_5$ by hydrogen and those by Upadhya[5] for reduction of Al$_2$O$_3$-CaO-SiO$_2$~5%PbO lead slags by iron-carbon alloys. However, given that Upadhya chose to ignore the important reaction between metallic iron and slag then his conclusions are probably invalid.

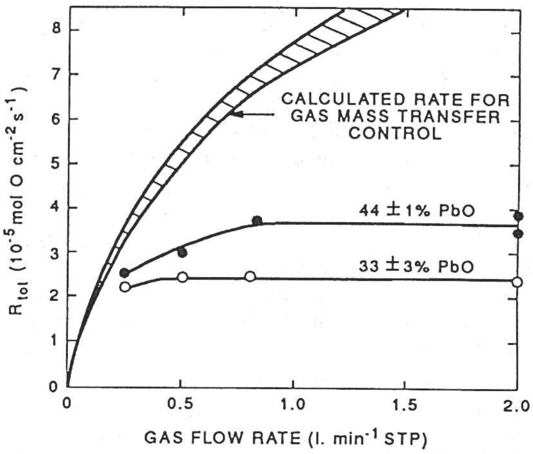

Figure 3: Variation of the measured and calculated (shaded area) total reduction rates (R_{tot}) of fluxed high lead ISASMELT slag with gas flow rate.

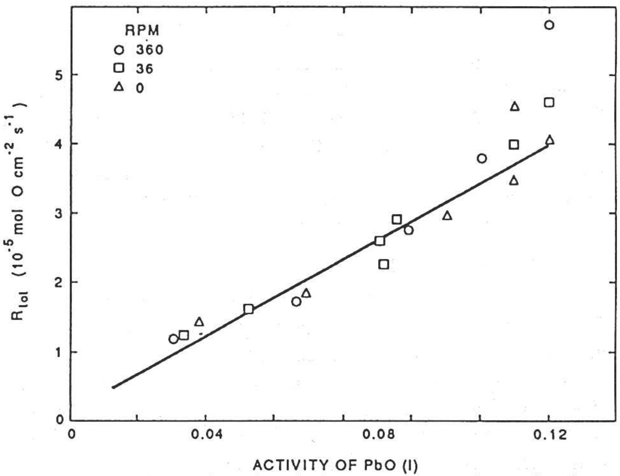

Figure 4: Effect of melt stirring speed on the reduction rate of zinc free, high lead slag at 1220 °C by CO-50% CO$_2$.

The activity of PbO (a_{PbO}) was calculated using a regular solution model developed by the authors[8].

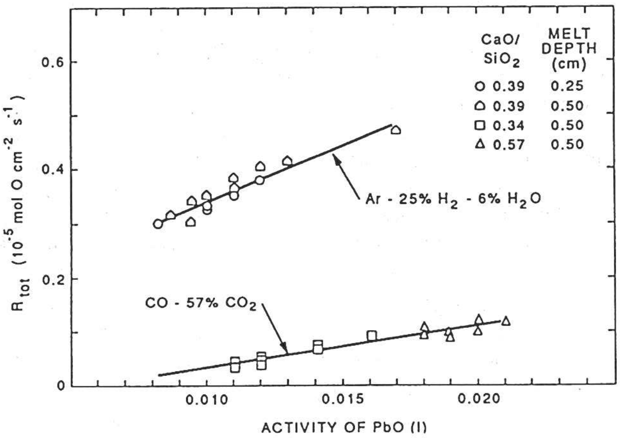

Figure 5: Effect of reductant type on the reduction rates of fluxed low lead ISASMELT slag at 1215±10°C.

Little is known of the relative rates of adsorption/desorption of CO or CO$_2$ on the surface of lead slag. The available surface tension data on lead slags is limited to those of binary lead silicates and lead borate melts and in lead silicates the surface tension of melts tends to *increase* with increasing silica concentration[10]. In order to verify the relative importance of this behaviour use was made of soda and sodium phosphate as additives, as they are among the most surface active oxides in iron oxide containing slags[11]. Thus if the adsorption/desorption phenomena played a predominant role in the reduction kinetics of these slag a marked ***decrease*** should arise from additions of small quantity (2-4 wt%) of soda or sodium phosphate. The results from these experiments showed quite the opposite behaviour, i.e. the reduction rates ***increased*** markedly. Similar behaviour was found for lead free synthetic zinc slags where various additions of soda were made. These findings are not consistent with adsorption/desorption at the gas-slag interface being the rate controlling mechanism. They suggest that the rates of adsorption of CO and desorption of CO_2 are sufficiently fast at the slag interface (both in ISASMELT slag and in synthetic zinc slags) so that other mechanism(s) control the overall reduction rates. It is worth pointing out that Pal *et al.* used hydrogen to reduce their iron free slags. These conditions are distinctly different to those used in the present study and are thought to be the cause of difference in the results obtained. Furthermore Belton[12] and Sun[13] have provided an alternative expalantion for the effect of strongly surface active and acidic oxide, such as P_2O_5, which involves dissociation of charged adsorbed species as the rate limiting step.

Recent studies by Belton and co-workers[14-16] and by Ban-ya and co-workers[17-20] on the interfacial rates of reaction of CO-CO_2 mixtures with various liquid iron oxide containing slags have provided a body of knowledge on the kinetics of oxidation/reduction reactions under conditions where mass transfer was not a limiting factor. Despite the differences in the experimental techniques employed by these independent groups of workers, their results are consistent in many respects. Their interpretations provide considerable evidence in support of the rate of formation of CO_2 at the gas-slag interface being rate controlling during the reduction of iron containing slags with CO or CO-CO_2 gas mixtures, i.e:

$$CO\,(g) + (O)_{slag} = CO_2\,(g) \qquad \text{... (2)}$$

For which the total reduction rate (R_{tot}) was expressed as:

$$R_{tot} = k_{app}\,(p_{CO} - p_{CO}{}^{e}) \qquad \text{... (5)}$$

or $$R_{tot} = k_{app}\,(p_{CO} - p_{CO_2}/a_{(O)}) \qquad \text{... (5a)}$$

where; p_{CO} and p_{CO_2} 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 melt (not activity of oxygen ions O^{2-}), with respect to unit CO_2/CO ratio as standard state.

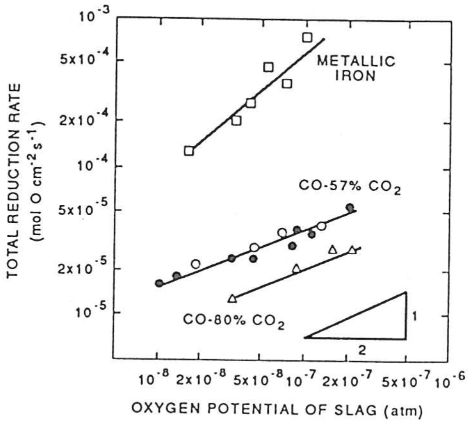

Figure 6: Dependence of the total reduction rate (R_{tot}) on the calculated oxygen potential of the slag and reductant type.

Based on the fact that the reaction has simple dependence on the Fe^{3+}/Fe^{2+} ratio, Belton *et al.* have postulated that in melts which exhibit significant semiconductivity, charge transfer between the melt and a charged species such as $CO_2{}^{2-}$ could be determining the rate of formation of CO_2 according to the following reaction mechanisms:

$$CO\,(g) + (O^{2-})_{slag} = CO_2{}^{2-}{}_{(ads)} \qquad \text{... (6)}$$

$$CO_2{}^{2-}{}_{(ads)} + 2(Fe^{3+})_{slag} = 2(Fe^{2+})_{slag} + CO_2\,(g) \qquad \text{... (7)}$$

If this mechanism was responsible for limiting the rate of reduction of lead slags by carbonaceous reductants, then the rate should be strongly dependent on the ability to transfer electrons between the slag and the reductant. The findings from experiments where the barrier for the charge transfer between the slag and reductant was "removed", or the electrical conductivity of the slag was varied by changing the concentrations of the charge transfer media (Fe^{3+} and Fe^{2+} contents) in the melts are summarized in Figures 6 and 7.

It is evident from Figure 6, that at a given oxygen potential in the slag, the reduction rate is considerably faster when metallic iron is used as reductant, i.e. when the transfer of electrons between the slag and reductant takes place more easily. Studies by Brimacombe and Richardson[21] and Prange *et al.*[22] provide evidence that rates of chemical reactions between metal and slag phase are extremely rapid and are about two orders of magnitude greater than the measured initial rates of solute transfer between metal and slag/molten salt. Furthermore, if the dependence of exchange current density with iron concentration found by Prange *et al.* is the same for these high lead slags, then for the iron concentration of ISASMELT slag, i.e. about 1.25×10^{-2} mol.cm^{-3}, the expected rate would be about 2×10^{-3} mol.cm^{-2}s^{-1}. This value is several times greater than that measured for the initial reduction rate of PbO by metallic iron. Thus it is reasonable to expect that kinetics of reduction of these slags by ***metallic iron*** is most likely controlled by mass transfer in the slag phase.

The equilibrium constant for the reaction;

$$(PbO) + CO\,(g) = Pb + CO_2\,(g) \qquad \text{... (8)}$$

would be about 500 at 1220 °C[23]. Accordingly, the CO_2/CO ratios ($a_{(O)}$) in equilibrium with lead metal and slags with a_{PbO} of 0.04 and 0.2 would be about 20 and 100, respectively. Therefore, when such slags are exposed to a CO-57%CO_2 gas mixture, the equilibrium partial pressure of CO ($p_{CO}{}^{e}$) at the gas-slag interface should be about 0.0285 and 0.0057 atm., respectively. It follows that when CO rich gas mixtures react with lead slags containing 10 to 50% PbO (a_{PbO} ~ 0.04 to 0.2) the rate of back reaction would be comparatively small and for practical purposes the rate equations (8) and (5a) can be simplified to:

$$R_{tot} \simeq k_{app}\, p_{CO} \qquad \text{... (9)}$$

Thus if the reduction rate of lead slags was limited by the rate of formation of CO_2, then the total reduction rate should be proportional to the partial pressure of CO in the gas phase. In Figure 6 the variation of R_{tot} with the oxygen potential of slag (pO_2) at 1220 ±10°C for two CO-CO_2 gas mixtures is shown. According to these results at a given pO_2, the R_{tot} almost doubled as the p_{CO} in the reducing gas increased from 0.2 to 0.43 atm.

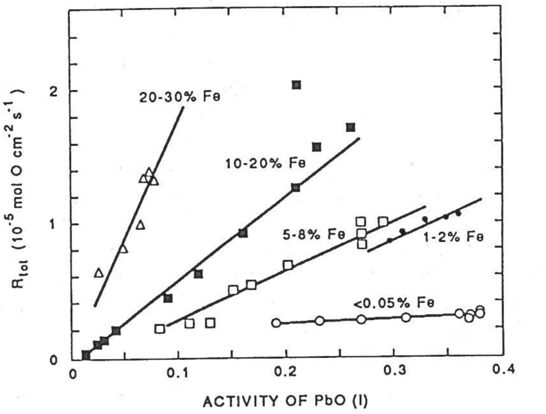

Figure 7: Effect of iron content of the slag on the total reduction rate (R_{tot}) of zinc free slags by CO-50%CO_2 at 1220±10 °C.

The results shown in Figure 7 are for conditions where the electrical conductivity or charge transfer within the slag and/or between the slag and reductant (CO-CO_2 in this case) was gradually lowered by reducing the transition metal content of the slag. It is evident that the reduction rate is considerably affected by the iron content of the melts. Since both the lead and total reduction rates showed similar dependence on the iron content of the slags, the results indicate that there is good coupling between the lead oxide reduction and the ferric-ferrous redox reaction:

$$Pb^{2+} + 2Fe^{2+} = Pb + 2Fe^{3+} \qquad \text{.. (10)}$$

Figures 4, 5 and 7 show that R_{tot} is strongly dependent on the a_{PbO}. With the exception of the results for "iron free" slags, R_{tot} is proportional to the a_{PbO} in the slag phase. Since the a_{PbO} is also a measure of the oxidation state of the slag, then the apparent dependence of R_{tot} on the a_{PbO} could be merely a reflection of the dependence of k_{app} on the oxidation state of the slags.

In the case of virtually iron free slags, R_{tot} is not proportional to the a_{PbO} or the oxidation state of the slag. These rates are slower than those obtained from iron containing slags. Since in the absence of a transition metal oxide in slags, the semi-conductivity behaviour of melts will be significantly reduced, then it is likely that other rate controlling steps such as transport of species in the slag become predominant. This is consistent with the findings from a number of investigations[24-26] on slags free of transition metals.

As discussed previously, when H_2-H_2O-Ar mixture was substituted for CO-CO_2, the total reduction rate was found to be considerably faster. Since the rate of formation of H_2O is likely to be considerably faster than that of CO_2[27], then this finding provides additional support to the proposal that rate of formation of CO_2 at the gas-slag interface being the rate controlling step in the reduction of iron containing lead slags by carbonaceous reductants.

In essence, the evidence presented above is consistent with the idea that reduction of ISASMELT slag and synthetic lead slags by ***carbonaceous reductants*** is controlled by the rate of formation of CO_2 at the gas-slag interface.

Dependence of the Apparent Rate Constant for Reduction on the Slag Chemistry and Temperature

In Figure 8 the calculated values of the k_{app} according to equation (5a) are plotted against the oxygen activity in slag ($a_{(O)slag}$). This Figure shows that at a given temperature the values of k_{app} are strongly dependent on the $a_{(O)}$ and the iron oxide content of the melts. Within the scatter of data, close agreement with a slope of unity is also apparent for most data sets. At a given $a_{(O)slag}$, the value of k_{app} was found to be dependent on the CaO/SiO_2 ratio as well as the Fe/SiO_2 ratio and the ZnO content of the slag. Also shown in Figure 9 are the values of k_{app} deduced from isotope exchange studies [14] on lime saturated calcium ferrite and calcium iron silicate (18% CaO, 29% FeO_x and 52% SiO_2) melts [15] at temperatures close to 1220 °C. It is interesting to note that exprapolation of the present results to low oxygen activity in the melt (i.e. low PbO contents) gives values for k_{app} which are close to the isotope exchange studies on calcium iron silicate slags with comparable CaO/SiO_2 ratio. This dependence of k_{app} on the oxidation state of lead slags is likely to be due to the strong effect that PbO has on the Fe^{3+}/Fe^{2+} ratio of slag at a given oxygen potential[28], as well as its effect on slag basicity.

The results obtained on ISASMELT slags containing strong basic oxides such as Na_2O also show similar behaviour with respect to k_{app}. The effect of strong basic oxides, such as soda, which are also surface active in iron oxide containing melt, could have a two fold effect.

Results from reduction of synthetic (zinc free) lead slags at temperatures in the range of 1180 to 1320 °C show that at a given oxidation state of slag, the k_{app} nearly doubles for every 45 °C rise in temperature. Given that for these slags the contribution of the PbO loss (i.e. reduced to Pb and volatilised as PbO) accounts for 70 to 90% of the total reduction rate, and that the vapour pressure of PbO increases by about 50% for a similar increase in temperature, then the activation energy associated with the reduction of lead slags is about 30 kcal mol^{-1}. This value is similar to those reported for the rate of formation/dissociation of CO_2 on iron silicate and calcium iron silicate slags[15].

CONCLUSIONS

Measurements of the rates of reduction of magnesia saturated ISASMELT slag (Al_2O_3-CaO-FeO_x-MgO-PbO-SiO_2-ZnO) and synthetic lead slags (CaO-FeO_x-MgO-PbO-SiO_2) by impinging a stream of CO-CO_2 gas on a thin layer of slag (3-10 mm) were made at temperatures in the range of 1180-1320 °C. These experiments were carried out under conditions where mass transfer in the gas or slag phase was not the rate controlling step. The results show a strong dependence of the reduction rate upon the;

- oxidation state of slag,
- partial pressure of CO in the reducing gas mixture,
- temperature and chemistry of the slag phase.

The experimental findings indicate that when CO-CO_2 mixtures are used as reductant, the rate of formation of CO_2 at the gas/slag interface is most likely to be the rate controlling step under the above conditions. In experiments where this barrier was "removed" by use of other reductants (e.g; metallic iron or H_2-H_2O gas mixture) considerable increase in the reduction rates of slag was observed.

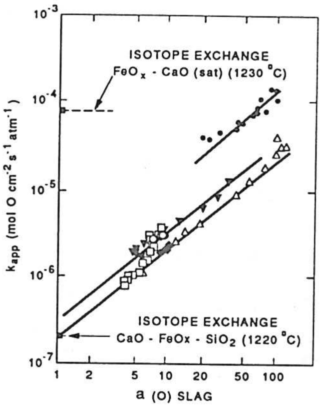

Figure 8: Dependence of the apparent rate constant (k_{app}) on the oxidation state of slag ($a_{(O)}$) for various slag compositions studied at 1220±10 °C. (● ; $CaO/SiO_2 = 0.55$, $Fe/SiO_2 = 1.67$, $ZnO = 9$-14%, ▼ ; $CaO/SiO_2 = 0.11$, $Fe/SiO_2 = 1.57$, $ZnO = 10$-20%, ☐ ; $CaO/SiO_2 = 0.33$, $Fe/SiO_2 = 1.03$, $ZnO = 10$-18%, ○ ; $CaO/SiO_2 = 0.82$, $Fe/SiO_2 = 1.24$, $ZnO = 10$-16%, ◆ ; $CaO/SiO_2 = 0.85$, $Fe/SiO_2 = 1.00$, $ZnO = 10$-17%, Δ ; $CaO/SiO_2 = 0.48$, $Fe/SiO_2 = 0.40$, $ZnO = 0\%$)

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