1. Introduction

An understanding of slag/carbon interactions is of great significance due to their extensive application in a number of metallurgical processes, especially in the blast furnace ironmaking process. One of the major advancements in the blast furnace technology has been the injection of pulverised coal through tuyeres to partially replace metallurgical coke as a source of heat and reductant. High injection rates for the pulverised coal (PCI), desirable for increasing the efficiency of the furnace, can seriously affect furnace stability with an increasing amount of unburnt char entering the blast furnace burden.1–3) After the unburnt char leaves the raceway, it could either be partially consumed within the furnace or escape along with the off-gases from the top of the furnace. The accumulation of unconsumed char within a blast furnace is a major concern as it can adversely affect the permeability in the burden and therefore the stable operation of the furnace. The consumption of unburnt residual char can take place through reactions with the metal, slag and gaseous phases. It would be ideal for the unburnt char to actively participate in ore reduction reactions, consequently replacing some more of coke and also reducing high levels of unburnt solids in top off-gases. The main focus of this study is on the interactions of char with the slag phase specifically reactions and wetting, as current understanding of these processes between blast furnace slags and carbonaceous materials is far from complete.

Blast furnace slags are comprised mainly of iron oxide, silica, alumina, lime etc. In the temperature range of interest, 1 500 to 1 700°C, iron oxide and silica are two main reducible oxides present in the slag. In addition, ash impurities present in char also contain iron oxide and silica to varying degrees and could participate in reduction reactions. Thomson et al.4) have reviewed the research carried out in the area of PCI with a special reference to combustion and coal/coke quality requirements. For a comprehensive understanding, they have pointed towards a need for a detailed study on the kinetics of slag/char interactions.

The kinetics of reactions taking place in the slag/carbon interfacial region was investigated at 1 500°C for a range of carbonaceous materials, namely synthetic graphite, natural graphite and two coal-chars. Two blast furnace slags, one rich in iron oxide and other rich in silica were used in this study. Slag/carbon reactions were studied in a horizontal tube resistance furnace in argon atmosphere, using the sessile drop approach. The volumes of CO and CO₂ evolved were obtained from an analysis of off-gases with the help of a mass spectrometer. These reactivity studies were supplemented with wettability measurements on these systems. With iron oxide rich slag 1, all carbonaceous materials showed non-wetting behaviour without much improvement with time. With silica rich slag 2, natural graphite and coal-chars showed dynamic wetting after some time. Synthetic graphite however continues to remain non-wetting. Reduction of iron oxide was a predominant reaction with slag 1 and reached completion for all carbon substrates. Reduction of silica, main reaction with slag 2, was however partial with considerable amounts of unreduced silica remaining behind even after 1 800 s of contact. Overall reaction rates in the initial stages of contact were quite similar for both graphites whereas both coal-chars showed relatively high reaction rates. These results point towards the important roles played by the chemical composition of slags and carbonaceous materials in reduction reactions.

KEY WORDS: slag; graphite; coal-chars; reactivity; wetting; blast furnace; pulverized coal injection.

Coal-char/Slag Interactions during Pulverised Coal Injection in a Blast Furnace: Reaction Kinetics and Wetting Investigations

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CO$_2$ + C = 2CO ...........................................(3)

These reactions involve diffusion of iron oxide from the bulk slag to the interface, chemical reactions at the slag/gas interface, diffusion of CO$_2$ to the interfacial region and participation in chemical reactions in the gas–carbon and liquid–carbon interfacial region. In the temperature range 1 300–1 500°C, Sarma et al. have investigated the reduction of FeO in smelting slags, containing less than 10% FeO with basicity of 1, by a range of carbonaceous materials. They have reported a small increase in reaction rates when coke was used as a reductant as compared to graphite and char and have proposed a mixed control model for overall reaction kinetics. Bafghi et al. have studied the effect of slag foaming and slag composition on the reduction of iron oxide in molten slag by graphite at 1 300°C. The reaction rate was significantly influenced by the slag composition. Mass transfer in the slag phase for slags with a basicity of 2 and chemical reaction at the interface for lower basicity slags were reported to be the rate limiting steps. Using vacuum suction, Bafghi et al. continuously removed CO gas generated by the iron oxide reduction. They observed that for initial FeO concentrations >2%, the indirect reduction by CO was less important than the direct reduction by graphite. Basically, the overall reduction rate is controlled by various steps in the series. For graphite, the rate limiting steps are liquid phase mass transfer and slag–gas reaction with gas–carbon reaction not playing a major role. For coke however, the considerably lower reactivity of coke towards CO$_2$ at high temperatures appears to cause this reaction to have a significant influence. Coal-chars however show a high reactivity towards gasification.

For silica reduction, the reaction between SiO$_2$ and C in powdery mixtures has significant rates from about 1 400°C onwards in vacuum or stream of argon. The reaction can be seen as a combination of two basic reactions:

\[ \text{SiO}_2 + C = \text{SiO} + \text{CO} \] ...........................................(4)
\[ \text{SiO} + 2\text{C} = \text{SiC} + \text{CO} \] ...........................................(5)

Overall reaction being

\[ \text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO} \] ...........................................(6)

There are two stable condensed phases coexisting in each reaction, i.e., SiO$_2$ and C or C and SiC. System freedom is 2 and temperature and partial pressure can determine the system. In the presence of molten iron, silicon transfer to iron could occur, according to the following reactions:

\[ \text{SiO} + \text{CO} = \text{Si} + \text{CO}_2 \] ...........................................(7)
\[ \text{SiO} + \text{C} = \text{Si} + \text{CO}_2 \] ...........................................(8)

Coke slag reactions are known to be responsible for generating SiO gas in a blast furnace. Croft has reported significant in situ reduction of silica in coke ash by carbon through the intermediate SiO gas phase and proposes this to be the main mechanism of silica reduction in the current blast furnace practice. Initially formed SiO(g) can be re-oxidised to silica during combustion which separates it from the other ash constituents and adds it in a pure and finely divided form to the ascending gas stream, from which it is filtered out by the descending coke bed. The actual reduction then takes place, as the metal runs over the impregnated coke picking up silicon at the same time as it dissolves carbon.

Ito and Tokuda have studied the reduction of silica in molten slag by carbon in the high temperature region of blast furnace, in relation to the partition of silicon among slag, metal and gas phases. They report that as a result of silica reduction, conditions for SiO evaporation are conducive in acidic slags, such as those with $a_{\text{SiO}_2} = 0.2$. Such slags would always be a source of SiO in the high temperature zone of blast furnace. On the other hand, basic slags, such as those with $a_{\text{SiO}_2} = 0.001$ (for example, CaO/SiO$_2$ = 1.5, Al$_2$O$_3$ = 15%) could always absorb SiO gas. Therefore, the composition of slag would be critical in dictating the behaviour of SiO gas in a blast furnace.

In our earlier work, we have observed that the wettability of carbonaceous materials by blast furnace slags is strongly influenced by the composition of the slag and the carbonaceous material. This study showed that when iron oxide content is low, the wetting behaviour is dictated by the extent of silica reduction in slag. Wetting was found to improve considerably with an increase in silica content. Wetting behaviour of slags containing high levels of iron oxide was however dictated by the deposition of reduced iron at the interface. In this paper, we report a detailed investigation on the influence of chemical composition of slag and carbonaceous material on the kinetics of reduction reactions taking place in the slag/carbon interfacial region at 1 500°C. These studies have been supplemented with wettability investigations on these systems.

2. Experimental Details

2.1. Materials Characteristics

Four carbonaceous materials, namely synthetic graphite, natural graphite and two chars were used in this study. Composition of carbonaceous materials is given in Table 1. Ash composition and relative content in natural graphite and coal-chars is given in Table 2. Synthetic graphite was in the form of a block, which was cut into slices of dimensions: 20×20×5 mm. These slices were then polished using emery papers up to 1 200 grit size (14 μm). Natural graphite was in the form of flakes and chars were fine powders (<38 μm). Natural graphite substrates were prepared by grinding graphite flakes as fine as possible in a ball mill to ensure homogeneous composition and then by placing a small amount of powder (~2 g) in a steel die (dimensions: 20×20×5 mm). The powder was then compacted in a hy-
draulic press under a load of 2 tonnes for 10 s. No binders were used in order to avoid unwanted contaminants or reactions. A similar procedure was used for coal-chars.

Slag compositions used in this investigation are given in Table 3. These blast furnace slags respectively had a simple basicity of 1.67 and 1.22. Experimental slags were prepared at 1600°C through a series of melting, crushing and remelting cycles to ensure complete homogeneity. Appropriate weights of oxides were mixed uniformly and melted in a muffle furnace. The oxide mixture was regularly stirred in the molten state. It was then quenched, crushed and ground to a fine powder in a ball mill. The process was repeated three times to ensure a completely homogeneous slag. Final product was chemically analysed for establishing accurate composition profile.

2.2. Experimental Details

Slag/carbon interactions were studied in a laboratory scale, horizontal tube resistance furnace using the sessile drop approach. A schematic diagram of the experimental set up is shown in Fig. 1. The furnace tube has an inside diameter of 50 mm. The furnace was fabricated from double walled, vacuum insulated stainless steel tubes fitted with a fan cooler to dissipate heat. The weight of the slag used was 0.20 g. Initially, the sample was held on a specimen holder, which could be pushed to the centre of the hot zone in the furnace with help of a stainless steel/alumina rod. The slag/carbon assembly was held in the cold zone of the furnace until the desired temperature (1500°C) was attained and equilibrated in the hot zone of the furnace. The assembly was inserted into the hot zone at the desired temperature of study; this eliminated any reaction that could occur at lower temperatures and possibly influence the phenomena to be studied at the temperature of interest. The furnace tube was purged with argon throughout the duration of the experiment. Argon flow rate was controlled by a mass flow meter. Using a mass spectrometer, the CO and CO₂ concentrations in the outlet gas mixture were analysed to determine the rate of the reaction. A series of blank runs were also conducted on carbonaceous materials without any slag. The volume of CO and CO₂ evolved was obtained from off-gas analysis, which was then converted to number of moles using standard gas equation. Data collected during blank (carbonaceous materials without slag) runs was subtracted from the data obtained using both slag and carbonaceous material. Assuming that the contribution to off-gases from carbonaceous material due to adsorbed oxygen and in-situ reactions remains unaltered in both cases, an attempt was made to isolate contributions coming just from carbon/slag interactions.

The wettability behaviour of the slag/carbon system was investigated using a closely controlled and visually monitored sessile drop technique. A high quality, high resolution charge-coupled device (CCD) camera fitted with an IRIS lens was used to capture the live in-situ phenomena in the furnace. The output from the camera was channelled to a video cassette recorder (VCR) and a television (TV) monitor to record the entire process as a function of time. This allows specific images, displaying the contact between the slag and carbonaceous material, to be captured from the videotape, as a function of time, into a computer using a frame grabber. A time-date generator is used in the system to display the duration of the process. At the end of the run, the slag droplet was examined under a Scanning Electron Microscope (SEM) and analysed using EDS (Energy Dispersive Spectroscopy) for changes in composition or the formation of new reaction products. Specially designed computer software was used to determine the contact angle.
from the captured images, on the basis of a curve-fitting exercise. The details of this software are given elsewhere.\(^\text{17)}\) For a better understanding of reaction dynamics, contact angles were recorded up to 2 h in most cases.

3. Results

3.1. Wetting Behaviour of Carbon/Slag Systems

The wetting behaviour of slag 1 and slag 2 with carbonaceous materials was investigated at 1 500°C as a function of time and the results on contact angle measurements are shown in Figs. 2 and 3 respectively. Slag 1 generally showed non-wetting behaviour for all carbonaceous materials under investigation, with contact angles changing from 100–120 degrees to 80–100 degrees with time. Small improvement in wettability could be caused by the deposition of reduced iron in the interfacial region. However with slag 2, while synthetic graphite continues to remain non-wetting, natural graphite and chars showed dynamic wetting with contact angle decreasing rapidly after some time. The onset of dynamic wetting takes place after 3 000 s for natural graphite, 7 000 s for char 1 and 5 000 s for char 2. High temperature images of natural graphite with slag 1 and slag 2 after approximately 1 800 s of contact are shown in Fig. 4. Spreading of slag 2 droplet on the natural graphite substrate can be clearly seen.

3.2. Interfacial Reactions

A number of reactions involving the reduction of iron oxide and silica present in both slag and ash impurities, and the oxidation of carbon are expected to take place in the interfacial region. Parameters being measured in this experiment are the volumes of CO and CO\(_2\) in off-gases emerging from the furnace. Raw data collected during blank runs on carbonaceous materials without any slag was subtracted from the gaseous volume data generated from carbon/slag assemblies in an attempt to remove any contribution from the adsorbed gases and \textit{in-situ} reactions. Resultant gases...
can then be assumed to come only from carbon/slag interactions. Converting gaseous volume to the number of moles of oxygen removed, the results from slag 1 and slag 2 at 1500°C are shown in Figs. 5 to 8. For all carbonaceous materials under investigation, the reduction of FeO was complete for slag 1. While synthetic graphite contains no impurities, iron oxide and silica concentrations in natural graphite and char 2 are quite comparable. The concentration of these impurities in char 1 is approximately half the corresponding amounts for natural graphite and char 2. In general, there is a time delay of 40 to 60 s before the evolution of gases is recorded by the mass spectrometer. This delay was caused by the time required for gases to travel from the reaction site to the mass spectrometer. This aspect of time delay was ascertained by passing argon gas through the furnace and recording the time taken (40 to 60 s) by the mass spectrometer to respond. Data shown in Figs. 5–8 reflects this time delay.

Assuming that the reduction of Fe₂O₃ to FeO occurs quite rapidly, every mole of FeO reduced corresponds to 1 mol of oxygen removed. Similarly 1 mol of SiO₂ reduced corresponds to two moles of oxygen removed. Using oxygen removal data and mass balance, amounts of these two oxides remaining unreduced in the slag was computed as a function of time. Additional numerical details can be found elsewhere. These results are shown in Figs. 9–12. The results on iron oxide reduction (Figs. 9 and 10) show slightly different starting times in different cases. While the initial delay of 40–60 s is caused by mass-spectrometer, additional

![Graph 5](image5.png)

**Fig. 5.** The number of moles of O removed as a function of time, for slag 1 with synthetic and natural graphite at 1500°C.

![Graph 6](image6.png)

**Fig. 6.** The number of moles of O removed as a function of time, for slag 1 with coal-chars at 1500°C.

![Graph 7](image7.png)

**Fig. 7.** The number of moles of O removed as a function of time, for slag 2 with synthetic and natural graphite at 1500°C.

![Graph 8](image8.png)

**Fig. 8.** The number of moles of O removed as a function of time, for slag 2 with coal-chars at 1500°C.

![Graph 9](image9.png)

**Fig. 9.** Variation of %FeO during interaction of synthetic and natural graphite with slag 1.

![Graph 10](image10.png)

**Fig. 10.** Variation of %FeO during interaction of coal-chars with slag 1.
preferentially getting reduced due to thermodynamic composition of the interfacial region. In slag 1, with iron oxide dynamic system with continuous changes in chemical composition, there is not much change in wettability. Carbon/slag assembly however is a partial reduction of silica can be observed in all cases under investigation.

4. Discussion
4.1. Wetting Characteristics

Changes in contact angle can be explained in terms of free energy changes associated with interfacial reduction reactions of Fe$_2$O$_3$ and SiO$_2$. With solid carbon substrate being an active participant, these reactions are accompanied by changes in composition of the slag droplet and substrate along with the formation of new reaction products at the interface. While the depletion of SiO$_2$ and Fe$_2$O$_3$ in slag leads to an increase in surface tension, the reduction reactions lower the interfacial free energy. With two opposing factors operating during initial stages of contact, there is not much change in wettability. Carbon/slag assembly however is a dynamic system with continuous changes in chemical composition of the interfacial region. In slag 1, with iron oxide preferentially getting reduced due to thermodynamic considerations along with depletion of carbon and deposition of iron in the interfacial region, reduction of silica is rather inhibited. While the reduction of silica is only partial (Figs. 11 and 12), iron oxide gets completely reduced. The contact angle for slag 1 does not significantly depend on the type of substrate (Fig. 2). Reduction of iron oxide deposits a significant amount of Fe in the interfacial region which appears to dominate wetting characteristics.

For slag 2 however, which is rich in silica with very small levels of iron oxide, the situation is quite different. The reduction and depletion of silica at the interface sets up concentration gradients leading to increased rates of mass transfer from the bulk to the interfacial region. With the silica present in carbonaceous materials, in addition to silica present in the slag, also taking part in these reactions, the chemical composition of the substrate becomes quite important. As the reduction reactions at the interface slow down due to the depletion of carbon and deposition of SiC, supply of silica begins to exceed consumption, thereby continuously leading to a decrease in the interfacial tension. A small decrease in interfacial tension leads to large changes in contact angle, leading to the onset of dynamic wetting. The deposition of SiC at the interface can also improve wetting. The onset is slowest for char 1 containing small amounts of silica and does not take place for synthetic graphite containing no silica (Fig. 3).

4.2. Reduction Kinetics

Iron oxide is the main oxide getting reduced in interactions of slag 1 with various carbons under investigation. The slope of the linear portion of the graph (Figs. 5 and 6) in the initial period of reduction was used to calculate the reaction rate constant:

\[
K = \frac{S \cdot \rho_B}{W \cdot 100} \left(\frac{A}{V_S}\right)
\]

Where $K$ in mol · m$^{-2}$ · s$^{-1}$ is the reaction rate constant, $S$ the initial slope in mol · s$^{-1}$, $\rho_B$ the substrate density in kg · m$^{-3}$ and $W$ the molecular weight of FeO, $A$ the interfacial area of contact in m$^2$ and $V_S$ the slag volume in m$^3$. Overall reaction rates for iron oxide reduction with slag 1 are given in Table 4.

Table 4. Reaction rate constants for the reduction of iron oxide ($\times 10^{-2}$ mol · m$^{-2}$ · s$^{-1}$) at 1 500°C.

| Substrate | Graphite S | Graphite N | Char 1 | Char 2 |
|-----------|------------|------------|--------|--------|
| Slag 1    | 10.9       | 10.5       | 11.0   | 11.2   |

Reaction rate constants shown in Table 4 reflect trends similar to those observed in the wetting behaviour of these materials with slag 1. Wetting characteristics did not show any dependence on the type of carbonaceous material. Reaction rate constants for all carbonaceous materials are quite similar and comparable to the rates quoted in literature for smelting slags. These results are in an excellent agreement with the results of Davies et al. and Sugata et al. that the reaction rate for iron oxide reduction to be generally independent of the type of carbonaceous material. They have concluded that mass transfer in the slag phase is the most likely predominant rate-controlling step. The reaction rates for chars are slightly faster than for graphites and

![Graph 1](image1.png)

![Graph 2](image2.png)
could be due to faster rates for the Boudouard’s reaction in the case of chars.11)

Overall reaction rate for silica reduction taking place during interactions of silica rich slag 2 are given in Table 5 using Eq. (9) with $W$ representing the molecular weight of SiO$_2$. The reaction rate constants and overall rates quoted in Tables 4 and 5 were calculated from the gaseous data collected during the first 200–300 s of contact. The effect of slag 2 on coal-chars is also quite significant as indicated by very high rates for both coal-chars. These results are in good agreement with Patalsky12) who had observed that the reactivity of carbon to SiO(g) increases with decreasing coal rank for bituminous coals. The rate of reduction of silica as quantified by Table 5 shows that chars have a faster rate as compared to graphites. This could be attributed to higher rates of Boudouard reaction in the case of chars as compared to graphites.13) These results show that the gasification of carbon plays an important role in the reduction of silica. Similar rates for graphites also support this view.

As the onset of dynamic wetting of natural graphite and coal-chars at 1500°C occurs after the reduction reactions have reached a steady state, wetting does not appear to play an important role in reaction kinetics at 1500°C. During the first 600–700 s when the reactions are observed, wetting characteristics are quite similar for all systems under investigation. Most contact angles during this period are in the range 100–200 degrees. After the initial reactions have slowed down, the wetting phenomenon appears to be related to the extent of silica reduction. As seen from Figs. 7 and 8, the extent of silica reduction demonstrates the following trend: Natural Graphite > Char 2 > Char 1 > Synthetic graphite. Greater the extent of silica reduction, greater is the deposition of reaction products such as SiC at the interface. It has been suggested that the presence of SiC in the interfacial region improves the wetting behaviour of slags.14) The time required for the onset of dynamic wetting follows a similar trend as that observed for the extent of silica reduction: Natural Graphite > Char 2 > Char 1 > Synthetic graphite (no dynamic wetting).

5. Conclusions

The influence of carbonaceous material and slag composition on reaction kinetics and wettability at the carbon/slag interface has been investigated. Two blast furnace slags, with a basicity of 1.67 and 1.22 respectively, and four carbonaceous materials, namely synthetic graphite, natural graphite and two chars were used in this study. These measurements were carried out at 1500°C. The following conclusions can be made from this study.

(1) With iron oxide rich slag 1, all carbonaceous materials showed non-wetting behaviour with hardly any improvement with time. While synthetic graphite continues to remain non-wetting with silica rich slag 2, natural graphite and coal-chars showed dynamic wetting after some time. The onset of dynamic wetting took place after 3 000 s for natural graphite, 7 000 s for char 1 and 5 000 s for char 2.

(2) Reaction rates as measured by the volumes of CO and CO$_2$ gas in off-gases, showed a wide variation for various slag and carbon substrate compositions. Reaction kinetics of both iron oxide and silica reduction was investigated. While slag 1 was iron oxide rich, slag 2 contained high levels of silica.

(3) Reduction of iron oxide was the predominant reaction of slag 1 with carbonaceous materials and silica reduction was inhibited and partial. Reaction rate constants for all carbonaceous materials are quite similar and comparable to the rates quoted in literature for smelting slags. Wetting characteristics also did not show any dependence on the type of carbonaceous material used as a substrate.

(4) With negligible levels of iron oxide, silica reduction was the predominant reaction for slag 2. Overall reaction rates in the initial stages of contact were quite similar for both graphites, both coal-chars showed relatively high reaction rates. As these rates were measured before the onset of dynamic wetting, these results point towards the intrinsic reactivity of these materials with silica rich slag as wetting is not expected to play an important role at this stage.

(5) At 1500°C, the onset of dynamic wetting takes place much after the reduction reactions have reached a steady state, as a result of deposition of reaction products in the interfacial region.

(6) These results indicate the important role played by the chemical composition of slags and carbonaceous materials in reduction reactions.

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