SLAG/CARBON INTERACTIONS AT HIGH TEMPERATURES DURING PULVERISED COAL INJECTION IN A BLAST FURNACE

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ABSTRACT

The practice of pulverised coal injection (PCI) in modern blast furnace ironmaking is gaining increased importance worldwide. One of the factors that could limit the maximum rate of coal injection is the accumulation of unburnt char within the blast furnace, due to incomplete combustion. Consumption of this unburnt char in the blast furnace could result in achieving increased PCI rates. The Co-operative Research Centre (CRC) for Black Coal Utilisation in Australia, is engaged in several projects to develop an understanding of the possible modes of consumption of the unburnt char within a blast furnace, through investigation of the interaction of different carbonaceous materials with slag, metal and gas phases.

This paper presents some of the results of the investigation of slag/carbon interactions, studied in terms of the wettability at the slag/carbon interface. Influence of temperature on the wettability at slag/carbon interface has been investigated by measuring the variation of dynamic contact angle with time, at three different temperatures, 1500°C, 1600°C and 1700°C for a blast furnace slag composition interacting with various carbonaceous materials, including graphite and chars.

The study has shown that an increase in temperature generally results in improved wettability at the slag/carbon interface. The wetting behaviour of the slag on different carbonaceous materials can be explained on the basis of the changes in the interfacial energy during the interaction. An increase in temperature is associated with a greater decrease in interfacial energy due to an increased extent and rate of the reduction reactions and a decrease in surface tension of the slag. This paper discusses the wettability of various carbonaceous materials by the slag at different temperatures and the associated phenomena.

1. INTRODUCTION

Slag/carbon interactions have been a subject of great interest due to their extensive application in a large number of metallurgical processes. The study is particularly relevant to the ironmaking processes, including the blast furnace ironmaking process. In spite of the stiff challenges from more recent ironmaking processes involving direct reduction, the blast furnace technology of ironmaking still remains the primary method of production of iron. However the technology has undergone developments that are aimed at improving the productivity of the process and reducing the environmental problems associated with the production of coke. One of the major advancements in the blast furnace ironmaking process has been the injection of pulverised coal through the tuyeres. Pulverised coal (PC) is now being extensively used as a tuyure injectant to partially replace metallurgical coke as a source of heat and reductant.

One of the important objectives in the current blast furnace ironmaking is implementing as high a pulverised coal injection (PCI) rate as possible, without affecting the furnace stability. Increased rate of PCI, however, imposes limitations on the stability of blast furnace operations. Generally, with increasing PCI rates, there is an increasing amount of unburnt char entering the blast furnace burden, if the burnout efficiency of the injected coal does not increase substantially. After the unburnt char leaves the raceway, it may

- be consumed within the furnace, and/or
- remain accumulated inside the furnace, and/or
- escape along with the off-gases from the top of the furnace.

The accumulation of the char within a blast furnace is a major concern, since it could adversely affect the permeability in the burden and therefore the stable operation of the furnace. The consumption of the unburnt or residual char could be through various phases including the metal, slag and gas phases. It would be desirable for the unburnt char to participate in reactions including ore reduction reactions, thereby minimising the extent of unburnt solids in the top gases. The main focus of this project is on the consumption of carbon in the char by the slag phase. The possible mechanisms by which unburnt char could be consumed through the slag phase include the consumption of carbon in the char in the reduction of slag and consumption of both carbon and ash in the char in the *in-situ* reduction of the char ash.

Study of slag/carbon interactions is important to understand the consumption of unburnt char by the slag phase within the furnace. The slag/char interactions can be characterised in terms of the wetting of the char by the slag and the char reaction kinetics during interaction with the slag phase. This paper describes the results of the research carried out on wettability studies of slag-carbon systems, specifically the influence of temperature in the range 1500°C-1700°C, while using various carbonaceous materials including graphites and chars.

2. PCI AND WETTABILITY

Wettability is a surface phenomenon that is a measure of the interaction between two phases. It is of utmost relevance in understanding the kinetics of heterogeneous reactions between two phases.

Surface/interfacial tension of the two phases will dictate their interaction and affect the wettability. The surface tension could be significantly influenced by the composition of the slag due to the presence of constituents such as SiO_2, CaO and S.

The interfacial phenomena between slag and char could play a major role in determining the consumption of the unburnt char through the slag phase, since it could dictate the kinetics of the reduction reaction and/or the interaction by virtue of the interfacial area of contact between the slag and the char. The interfacial phenomena may be understood from the investigation of the wettability of the chars by the blast furnace slags.

Different parameters are used to characterise the wetting of a liquid on a solid. The most commonly used parameter is the contact angle, θ, a characteristic angle formed at the solid-liquid-gas interface as a result of the intermolecular forces acting on the liquid drop. Complete or spreading wetting is said to occur when the contact angle is 0°. In this case the liquid spontaneously spreads over the solid surface. At the other extreme, complete non-wetting could occur if the contact angle is 180°. Fig 1 illustrates the conditions of non-wetting and complete wetting for a drop of liquid resting on a solid surface. Generally speaking, non-wetting is considered to be the condition when the contact angle is greater than 90° [1].

The contact angle is linked to surface energies by Young's equation [2] as follows.

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} . \cos \theta \qquad (1\text{-}1)$$

or

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \qquad (1\text{-}2)$$

where γ_{sv} , γ_{sl} and γ_{lv} refer to the interfacial tensions at solid-vapour (or gas), liquid-solid and liquid-vapour (or gas) interfaces respectively and θ is the contact angle. The term γ_{lv} is referred to as the free surface energy or surface tension of the liquid. As is clear from Equation 1-2, the contact angle of a given liquid depends on the value of γ_{sv} - γ_{sl}, a factor which is called the driving force for wetting [3]. The degree of wetting is controlled by the relative values of the interfacial energies. According to Pask [4], if the solid substrate actively participates in a chemical reaction at the interface, the specific Gibbs free energy of the reaction at the droplet/solid interface per unit area and unit time, dG_R, can contribute to the driving force for wetting and therefore a decrease in contact angle. Pask [4] notes that the free energy change during the reaction contributes to the driving force for wetting only when the solid is an active participant in the reaction. For this to take place, the composition of the substrate must change, or it must react with the liquid.

In general, wetting improves with an increase in temperature, that is, the contact angle decreases. The magnitude of the change in wetting is a function of the type of system under consideration. In the case of non-reactive systems, with no chemical interaction at the interface, and when the wetting is primarily a function of the dispersive forces, the dependence of wettability on temperature is mainly the result of the variation of liquid surface tension with temperature. If the system, however, is reactive, then the temperature dependence could assume greater significance, due to the influence of the chemical interaction and free energy changes, in addition to the variations in surface tension. Systems in which a chemical reaction takes place, are often

characterised by a wetting threshold temperature, beyond which wettability increases rapidly [5]. Temperature could have a strong influence on the surface tension of the liquid phase and on the influence of surface-active agents in the system, regardless of the nature of the system, reactive or non-reactive. This could alter the wettability in a system significantly.

3. WETTABILITY OF CARBONACEOUS MATERIAL BY SLAG

There has been limited research done so far, aimed specifically at the wettability of solid carbon by liquid slag. Amongst the studies reported, Nakashima et al [6] reviewed the studies on wettability of materials including refractory and graphite by liquid slag. They report that, while liquid slags wet most refractories, they do not wet graphite. Towers [7] reports that the contact angle of a blast furnace slag on graphite decreases with time due to the reduction of silica at the interface. Addition of a small amount of SiC to the graphite and increase in the sulphur content of the slag has been observed to improve the wetting by the slag [8]. The reduction of silica and formation of SiC at the slag/graphite interface is believed to be responsible for the wetting of a graphite by such a slag.

According to Ebisawa et al [9] the formation of SiC at the slag-graphite interface seems to be closely related to the wetting characteristics. They also show that wettability increases with temperature and there seems to be a critical temperature between 1700°C and 1750°C above which spreading occurs rapidly. The sulfur content in the slag influences the wetting behaviour. The authors also report that the wetting behaviour of a slag is suppressed by the presence of MgO in the slag.

Wettability of carbonaceous materials by slags has also been studied by some investigators [10-12] using X-ray transmission technique to shed light on the slag foaming phenomena during smelting reduction. In their study, Zhang and Fruehan [10] attributed the anti-foaming effect of coke and coal-char to their non-wetting nature with CaO-SiO_2-CaF_2 slag.

The authors of this paper have previously reported [13,14] that the wettability of carbonaceous materials by blast furnace slags is strongly influenced by the compositions of the slag and the carbonaceous material. The study shows that when the iron oxide content in the slag is low, the wetting behaviour is dictated by the extent of silica reduction in the slag. Wettability could be expected to improve with increasing silica content. When the iron oxide content in the slag is high, the wetting behaviour could be dictated by the deposition of iron at the interface.

To summarise, there is limited literature available on the investigations on wettability of carbon by slags in terms of contact angle measurement, particularly for char-slag interactions which is the focus of the present study. A comprehensive understanding of the fundamentals of interaction between slag and char phases is essential to understand the behaviour of unburnt char in the blast furnace burden. The primary focus of this paper is on the interaction of the unburnt char with the blast furnace slag in terms of the wetting behaviour at the slag/carbon interface. The present work is carried out using high temperature systems, in accordance with the temperatures prevalent in the blast furnace during these interactions. Slag composition selected is typical of a blast furnace hearth slag, with a relatively low iron oxide content. Chars used are those produced in a

laboratory-based PCI rig. The wetting behaviour is characterised in terms of the dynamic contact angle at the slag/carbon interface, as a function of time.

4. PROCESS PARAMETERS

Slag/char interaction in a furnace during PCI is influenced by many variables. The present research work is focused primarily on the following process parameters described below.

4.1 Type of Carbonaceous Materials

Five chars, produced in the PCI rig at BHP Research Laboratories, Newcastle, Australia, were used for the study. The details of the PCI rig and the technology used for production of the chars are available elsewhere [15,16]. To form a basis for understanding and explaining the role of the mineral matter in the char in the interaction with the slag phase, wettability experiments were also carried out with two graphites, a synthetic graphite, Graphite S, containing 0.001% ash, and a natural graphite, Graphite N, containing 11.7% ash. The synthetic graphite was available in the form of blocks that could be cut to required size. Natural graphite was available in the form of flakes.

The carbonaceous materials used in the experiments were analysed for their compositions. Table 1 lists the different carbonaceous materials used in the study and their compositions. Table 2 lists the ash composition of these materials and their contents in the carbonaceous materials.

4.2 Blast Furnace Slag Composition

The slag composition studied is given in Table 3. The low iron oxide slag is representative of a typical slag in the hearth of the furnace.

4.3 Temperature and Furnace Atmosphere

The wettability experiments were carried out at three different temperatures $1500^{\circ}C$, $1600^{\circ}C$ and $1700^{\circ}C$. All the experiments were carried out under an inert gas atmosphere, consisting of high purity argon (99.9% purity).

5. EXPERIMENTAL METHODS

The slag/carbon interaction study was carried out in a laboratory-scale, horizontal tube furnace using the sessile drop wetting approach. The details of the experimental apparatus and method are given elsewhere [13,14]. The schematic diagram of the experimental set up is given in Fig 2. The furnace tube has an inside diameter of 50 mm. The sample is held on a specimen holder made of alumina, which is pushed to the centre of the hot zone in the furnace, with the help of an alumina rod. A holder used for the experiments is shown in Fig 3. The substrate of size 20x20x5 mm, is made of the carbonaceous material under study and the slag powder, of about 0.25g weight, placed on the surface. In the case of synthetic Graphite S, the substrate is sliced out of a solid

block of graphite. In the case of all other carbonaceous materials, Graphite N and the chars, the substrate is produced by compacting graphite flakes or pulverised chars, using a hydraulic press. The slag is prepared synthetically in a muffle furnace, using pure oxides as the starting materials. The iron oxide in the slag is present as Fe_2O_3. The details of the preparation of slag and the substrates are given elsewhere [13].

The slag/carbon assembly is held in the cold zone of the furnace until the desired temperature is attained and equilibrated in the hot zone of the furnace. The assembly is inserted into the hot zone at the desired temperature of study. This eliminates any reaction that could occur at lower temperatures and could influence the phenomena to be studied at the temperature of interest. The inert gaseous atmosphere, argon, is fed into the furnace from one end of the furnace. The flow rate of the inert gas (argon) is maintained constant at 0.6 litre/minute in all the runs, during the period of heating up the furnace and during the experimental run. The off-gases from the other end are channeled into a mass spectrometer for continuous on-line monitoring and analysis of the off-gas composition.

As shown in Fig 2, a high quality, high resolution CCD (charged coupled device) camera fitted with an IRIS lens is used to capture the live in-situ interfacial phenomena of the system in the furnace. The output from the camera is channeled to a VCR-TV monitor to record the entire process as a function of time. A time-date generator is used in the system to display the date and the duration of the process. The length of these experiments, and the video recording, is maintained up to two hours, to investigate the dynamic nature of the wetting behaviour. Specific images displaying the contact between the slag and carbon subtrate are captured from the videotape into a computer using a frame grabber. These images are captured periodically to study the variations with respect to time.

The stored images are analysed to determine the contact angle with the help of specially designed and developed computer software [17]. This software performs a curve fitting exercise through a systematic series of steps. The contact angles are determined at closer intervals of time up to 10 minutes after the melting of the slag. Thereafter, the contact angles are determined after every 10 minutes.

At the end of the run, the slag droplet and the graphite substrates are examined under a HITACHI S-4500 Field Emission Scanning Electron Microscope (FESEM), which is linked to an X-Ray Energy Dispersive Spectrometer (EDS). The slag droplets are subjected to EDS analysis to determine the final slag composition. Also, in these cases, the initial slag was studied using EDS in addition to the other analyses discussed earlier. For a number of runs, the slag crumbles on cooling to room temperature and mixes with the carbonaceous material, thereby eliminating the possibility of any EDS study. It has not been possible to conduct EDS at the slag/carbonaceous material interface. In all the cases with synthetic graphites as the substrates, the slag droplet does not adhere to the substrate. In the cases with natural graphite and the char substrates, where the slag droplet is adherent to the substrate, it is not possible to retain the substrate in the compact form after the run. It is therefore not possible to study the interface under the FESEM.

6. RESULTS

Measurement of dynamic contact angle was carried out as a function of time, for the slag on the various carbonaceous materials at the different temperatures. The results of the wettability studies conducted at various temperatures are given in the following sections.

6.1 Influence of Carbonaceous Materials at 1500°C

The wetting behaviour of the slag, as a function of the composition of the carbonaceous materials, is depicted in Fig 4 [14]. The slag demonstrates a dynamic wetting behaviour at 1500°C. In general, increase in the ash content in the carbonaceous material, particularly in the two graphites, improves its wetting by the slag. Graphite S and Char 4 display non-wetting behaviour with the slag. The slag droplet actually rolled off Char 4, due to the non-wetting behaviour, as a result of which contact angle measurement could not be continued. The slag also displays a non-wetting behaviour on Char 1 for a long period of time (over 90 minutes) after which the wettability starts to improve. On Graphite N and Chars 2, 3 and 5, the slag displays an initial non-wetting behaviour which starts to improve within a relatively shorter period of time for Graphite N (within 15-20 minutes) compared to that for Chars 2, 3 and 5 (within 45-60 minutes). The improved wettability of the higher-ash graphite and the chars suggests that the presence of ash in the carbonaceous material has a strong influence on the interaction. However, the relatively prolonged poor wetting of Char 1 and non-wetting behaviour of Char 4, as compared to Graphite N and Chars 2, 3 and 5, in spite of the high ash content of Chars 1 and 4, suggests that ash content alone may not dictate the wettability. Fig 5 a)-d) show examples of the high temperature images of the interaction, at similar times of interaction, of the slag with two graphites (S and N) and two chars (Char 1 and 2) at 1500°C displaying cases of poor wetting and good wetting. The times of interaction, that is the time of contact between the slag and carbonaceous material, in the form hours:minutes:seconds are also shown on the images.

6.2 Influence of Temperature

Figs 6 and 7 show the variation of the interfacial contact angle described by the slag on various carbonaceous materials at 1600°C and 1700°C respectively. The slag displays a dynamic behaviour on all the carbonaceous materials at these temperatures, similar to the behaviour displayed at 1500°C. However, the time taken to achieve good wetting decreases considerably with an increase in temperature. The slag spreads completely on the substrates at these temperatures, except on the synthetic Graphite S at 1600°C, although the wetting on Graphite S at 1600°C is better than the wetting at 1500°C. Char 1, which had displayed a poor wettability by the slag even up to 90 minutes at 1500°C, exhibits excellent wetting by the same slag within 11 minutes at 1600°C and within 5 minutes at 1700°C. Fig 8 displays the difference in the dynamic nature of the interaction of the slag on Char 1 at the three temperatures. Fig 9 shows the high temperature images comparing the wetting behaviour of the slag on Char 1 at 1500°C and 1600°C, 11 minutes after melting, displaying the improvement in wetting at 1600°C.

7. DISCUSSIONS

Generally, slags are reported to demonstrate a non-wetting behaviour on graphite and other forms of carbon [6,7,12,18]. However, reduction of silica and presence of SiC at the interface has been reported to result in an improvement in wetting of graphite by blast furnace slag, as a function of time [8,9]. The experimental results obtained in this study clearly indicate that the slag exhibits a dynamic wetting behaviour dependent on the type of carbonaceous material, the time of interaction and temperature.

7.1 Influence of Silica Content in the Carbonaceous Material

The slag/carbon interface could be assumed to comprise of a modifiedslag that consists of constituents from both slag and carbonaceous material. Accordingly, the silica content of the same slag increases at the interface, with an increase in silica content of the carbonaceous material. Towers [7] has reported a dependence of wetting behaviour of graphite by slag on the reduction of SiO_2 in the slag by carbon. With greater reduction of SiO_2, there is a larger decrease in the contact angle. Such a behaviour is observed in the case of the slag in this study. Influence of silicon carbide (SiC) at the interface on improving the wettability at the slag/graphite interface has also been reported elsewhere [8]. Measurements of CO gas generation during the slag/carbon interaction, in this study, show that the extent of reaction increases with increasing silica content in the carbonaceous material for the slag [13]. The contact angle measurements also show a similar dependence on the SiO_2 content in the carbonaceous material, for wettability with the slag, that is, the wettability improves with increasing silica content. This is plotted in Fig 10, which shows the variation of contact angle as a function of the silica content of the modified slag, after taking into consideration the contribution from the carbonaceous material. The composition of the constituents of the modified slag is calculated by assuming that the ash in the carbonaceous substrate, up to a certain depth, becomes a part of the liquid slag at the interface. The methodology and calculations used in the determination of this average composition are given elsewhere [13].

The changes in the contact angle observed for the slag as a function of the carbonaceous materials can be explained on the basis of free energy changes associated with the interfacial reduction reaction of primarily SiO_2 in the slag and of both SiO_2 and Fe_2O_3 in the ash (of the carbonaceous material) present at the interface [14]. These reactions are accompanied by a change in the composition of the slag and the substrate and formation of new products at the interface. Therefore, according to Pask [4], the solid carbon substrate is an active participant in the reaction and the free energy changes during the reactions contribute to reduction in the interfacial energy. However due to the reduction, and therefore the depletion of the oxides at the interface, there is an increase in the surface tension of the slag at the interface [19]. As a result of the two opposing factors, the free energy change decreasing the interfacial tension and the depletion of SiO_2 and Fe_2O_3 increasing the surface tension, there is no appreciable change in the contact angle during the slag/carbon interaction for a certain period of time from the initial contact. In the case of the slag in this study, the reduction of silica at the interface is appreciable, as observed from the off-gas analysis [13]. This could result in a significant concentration gradient between the bulk and the interface. This can lead to mass transfer from the bulk to the interface, which results in a continuous change in composition of slag at the interface. When the reaction occurs at a high rate for a certain period of time from initial contact, a negligible change

in contact angle is observed as explained earlier. However, as the reaction slows down due to depletion of carbon at the interface, the rate of supply of silica from the bulk to the interface exceeds the rate of consumption of the oxide at the interface. The interfacial tension at the solid/liquid interface therefore starts decreasing, resulting in a continuous decrease in contact angle as observed in Figs. 4, 5 and 7. With increasing time, as the contact angle drops, even a small decrease in interfacial energy is sufficient to cause significant decrease in contact angle. This is evident from the relatively earlier decrease in contact angle, shown in Fig 4, at times after 60 minutes since melting, for the good wetting cases of the slag on Graphite N and Chars 2, 3 and 5. This is in agreement with the observation made by Zelinski et al [3], who showed, for molten oxide glasses, that contact angle changes are very sensitive to small variations in interfacial energies, particularly for small contact angles, and that variations in interfacial energy of only a few percent could drastically change wetting interactions, by reducing the contact angle at the interface.

The EDS results of the slag droplet after 60 minutes into the wettability run indicate that the slag composition changes significantly when the slag/carbon interaction demonstrates good wetting, as is the case with the slag on Graphite N and Char 2. When the wetting is poor, as on Graphite S and Char 1, this change in composition is not as significant. This is shown in Table 4 [14]. FESEM analysis of the slag and the substrates at the end of the run provided evidences of reduction of SiO_2 at the slag/carbon interface [14]. Fig 11 shows an EDS spectrum of a particle observed on the surface of Graphite N after its interaction with the slag at 1500°C, after 60 minutes of interaction. As is clear this particle is rich in reduced Fe and Si. In comparison, the EDS spectrum of the surface of Graphite S, under similar conditions, shown in Fig 12, reveals mainly reduced Fe, indicating that reduction of SiO_2 is not as significant in the case of Graphite S as compared to Graphite N. Reduction of SiO_2 and Fe_2O_3, in the case of Graphite N, is promoted by increased concentration at the interface; due to increased SiO_2 and Fe_2O_3 content in the carbonaceous material. This is in accordance with the EDS analysis of the particles on the surfaces of the two graphites after their interaction with the slag, Graphite S showing lesser extent of reaction due to a lower SiO_2 content as compared to Graphite N. These evidences can explain the observed differences in wettability of various carbonaceous materials during their interaction with the same slag, and establish the significance of silica content in the carbonaceous material.

7.2 Influence of Temperature

The behaviour of the slags at the higher temperatures can be explained on the basis of the changes in interfacial energy due to the occurrence of reduction reaction and changes in surface tension. The surface tension of the slag has been measured using sessile drop approach at different temperatures, using platinum substrates, and the results are shown in Table 5. Increase in temperature generally brings about a reduction in the surface tension of the slag [19] as well as a greater free energy change due to an increase in the extent and rate of the reduction reaction. As a result, the changes in interfacial energies at higher temperatures are more rapid as compared to 1500°C.

Higher temperature results in an earlier decrease in contact angle for the slag on all the substrates, including Graphite S. The complete spreading of the slag on the substrates is a result of the decrease in interfacial energy brought about by an enhanced mass transfer of the constituents from the bulk to the interface at the higher temperatures. The greater the extent and rate of reduction at the interface, the more rapid the decrease in interfacial energy, and therefore the dependence on the silica content at the interface. Temperature has an influence on surface tension as shown in Table 5.

The results of the off-gas analysis show that there is an increased rate and extent of reduction of silica in the slag, with an increase in temperature. As a result, improvement in wetting in the case of the slag is noticed at an earlier time period at higher temperatures, and improvement in wetting is noticed on Graphite S, as well. In the case of Char 1, for example, on which the wettability of the slag improves more rapidly at the higher temperatures, the rates of reduction of silica increase from 26×10^{-6} moles.cm^{-3}.s^{-1} at 1500°C to 60×10^{-6} moles.cm^{-3}.s^{-1} at 1600°C and to 71.5×10^{-6} moles.cm^{-3}.s^{-1} at 1700°C [13]. Fig.13 shows variation in the time required for dynamic changes in the contact angle to commence during the interaction of Char 1 with the slag as a function of the rate of silica reduction at the three temperatures. This time required for dynamic changes in contact angle to commence, corresponds to the time when the graph starts to deviate from the initial nearly horizontal trend. The graph shows the rapid reduction in the time taken for the dynamic changes to occur with an increase in the rate of reduction.

Figure 14 displays a comparison of the variation of the time required for dynamic changes to commence during the interaction of various carbonaceous materials with the slag at the three temperatures, 1500°C, 1600°C and 1700°C. Graphite S is not shown at 1500°C and 1600°C, since there is no significant change in the contact angle of the slag on this substrate during the time of the experiment. Char 3 is not shown as measurement of contact angle of the slag on this substrate is limited to 1500°C only. Char 4 is not shown as the slag rolled off this substrate at all the three temperatures. As is observed from the figure, at the lowest temperature, the dynamic changes are a relatively strong function of the contribution of silica from the carbonaceous material. As a result, Char 1, which has about 4.43% SiO_2 as compared to a value of over 7% by Graphite N, Char 2 and Char 5, requires a relatively longer time for the slag to display dynamic changes in the contact angle. On Graphite S, which contributes practically no silica, the slag displays no significant dynamic changes. At the higher temperatures, the time required for dynamic changes to commence is not significantly influenced by the type of carbonaceous materials. However, on Graphite S, the slag displays relatively no dynamic changes even at 1600°C and the time for dynamic changes to commence is relatively higher at 1700°C compared to the other carbonaceous materials. This indicates that contribution of silica at the interface by the carbonaceous material is an important factor dictating the time of occurrence of dynamic changes in contact angle at the slag/carbon interface, particularly at 1500°C. In the absence of silica contribution by the carbonaceous material, the dynamic changes are less likely to occur even at relatively high temperatures, such as 1600°C. Char 4 is an exception as the slag displays poor wetting on this substrate at all temperatures, in spite of the presence of 4.19% SiO_2 in Char 4. At this stage, the non-wetting behaviour of Char 4 by the slag cannot be explained on the basis of silica content in the char.

8. CONCLUSIONS

Influence of the carbonaceous material and temperature on the wettability at slag/carbon interface has been investigated by measuring the variation of dynamic contact angle of a typical blast furnace hearth slag with time, at three different temperatures, 1500°C, 1600°C and 1700°C. The results of this study have shown that the wettability behaviour during slag/carbonaceous material interaction could be a function of the composition of carbonaceous material and temperature. The specific conclusions that can be made on the basis of the findings of this study and studies recently reported by the present authors [13,14], are as follows.

- The wetting behaviour is dependent on the composition of a modified slag at the interface, that is a combination of the slag and the ash present in the carbonaceous material. Wetting at the interface of the slag and the carbonaceous materials is dependent on the concentration of silica in the carbonaceous material.
- Increased silica content in the modified slag could improve wetting due to greater extent and rate of silica reduction. As a result the slag displays a more rapid rate of improvement of wetting with increasing silica content in the carbonaceous materials, such as Graphite N and Chars 2, 3 and 5. EDS analysis of the slag droplet and the carbonaceous substrate, after the runs, provide evidence of silica reduction during the slag/carbon interaction. It also shows a more significant change in composition, indicating greater extent of reduction, in the cases where the wetting is relatively good.
- An increase in temperature is associated with a greater decrease in interfacial energy due to increased extent and rate of the silica reduction and also with a decrease in surface tension of the slag. Increase in temperature accelerates the dynamic changes in contact angle, resulting in improved wetting with the carbonaceous materials at earlier times. This is attributed to an increased rate of reduction at higher temperatures. This is supported by an increased value of the rate of silica reduction for the same slag/carbon system at higher temperatures.
- Contribution of significant amount of silica by the carbonaceous material is one of the important factors influencing the time for the slag to display an improvement in wettability, at all temperatures. At 1500°C, the relative rate of improvement in wettability of the slag on various carbonaceous materials depends on the type of carbonaceous material, specifically its silica contribution. Higher the silica contribution by the carbonaceous material, the earlier is the change in wetting displayed by the slag. At the higher temperatures, the time of occurrence of improvement in wetting is relatively less influenced by the type of carbonaceous material. When the silica contribution is negligible, such as that by Graphite S in this study, the slag may display no significant change in wettability with time even at the higher temperatures of 1600°C. It may take a relatively longer time to display an improvement in wetting even at the higher temperatures of 1700°C, compared to silica-bearing carbonaceous materials.

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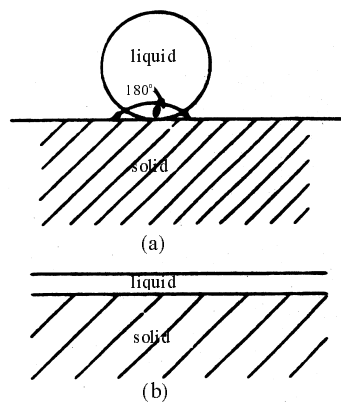19.   B.J. Keene, *Slag Atlas*, 2nd Edition. Verlag Stahleisen GmbH: 313-348, 404-511.

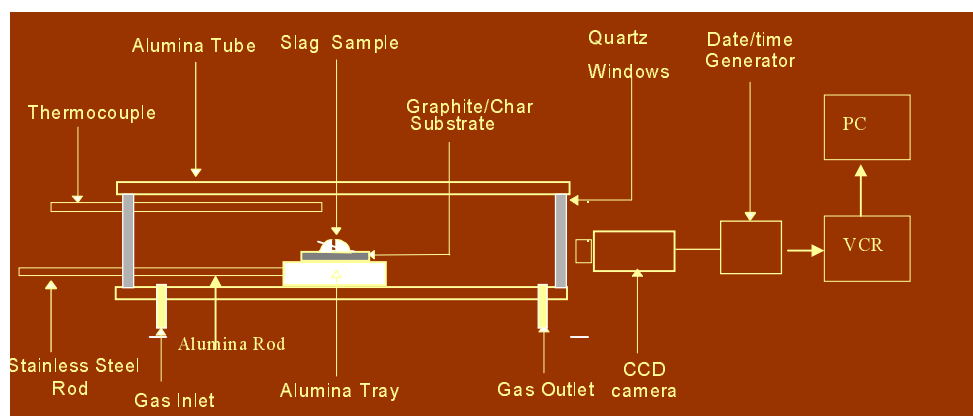*Figure 1 Conditions of (a) complete non-wetting and (b) complete wetting*

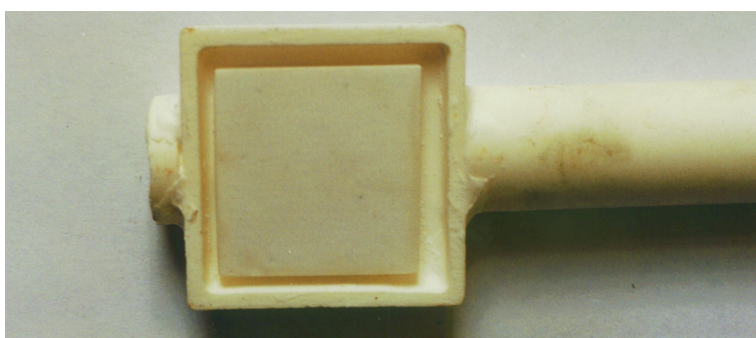*Figure 2 Schematic diagram of the experimental set up*

Figure 3 Holder used in the experiment, before insertion into the furnace
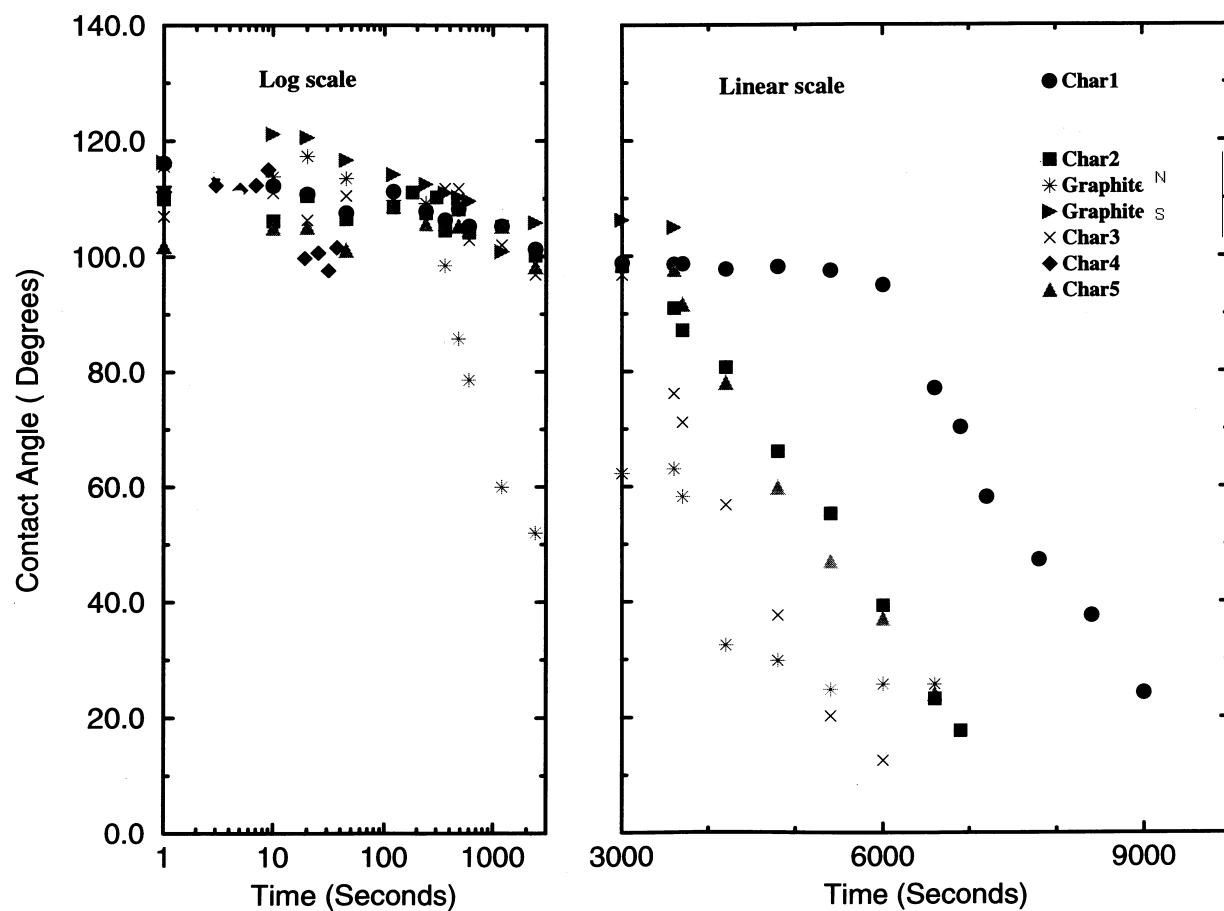
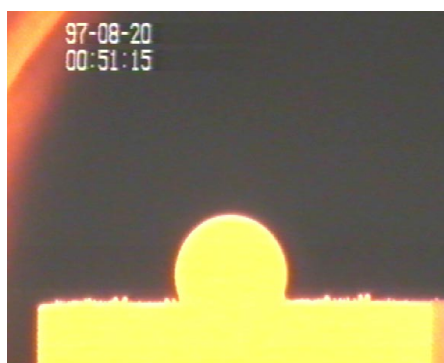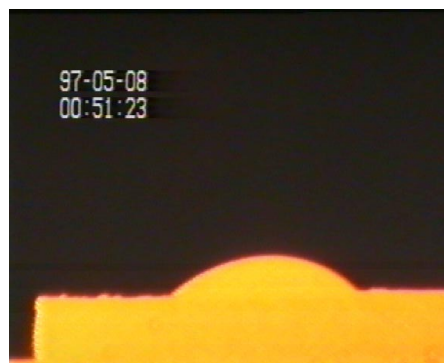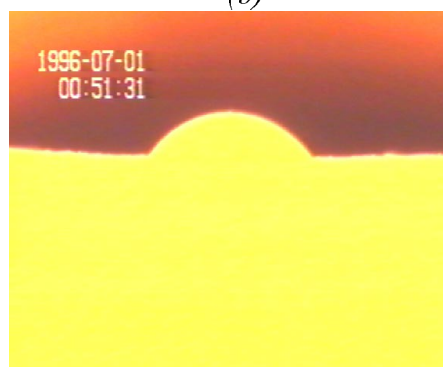*Figure 4 Variation of contact angles described by the slag on various carbonaceous substrates at 1500 °C, as a function of time*

Figure 5 High temperature images of the interaction of the slag at 1500℃ on (a) Graphite S, displaying poor wettability, (b) Graphite N, displaying good wettability, (c) Char 1, displaying poor wettability, and (d) Char 2, displaying good wettability. The times of interaction, that is time of slag/carbon contact, are shown on the images.
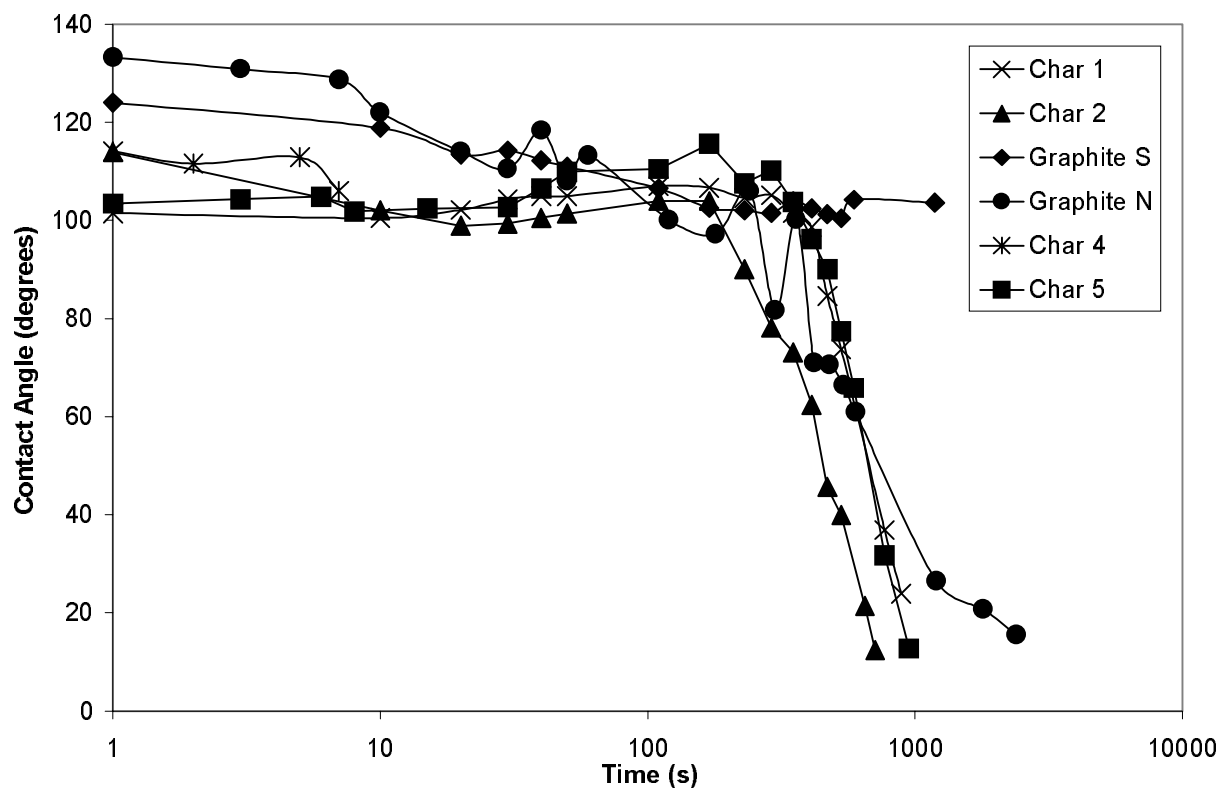
Figure 6 Variation of contact angles described by the slag on various carbonaceous substrates at 1600 °C, as a function of time
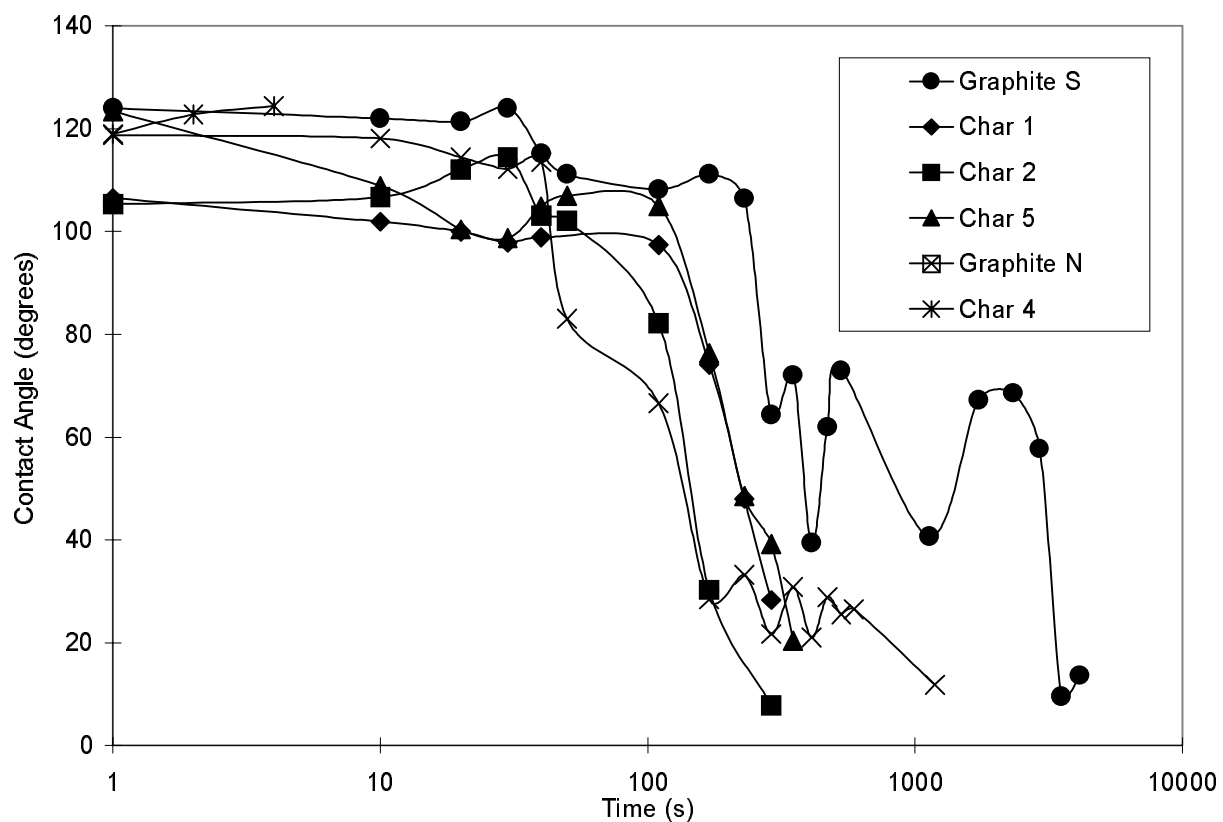
Figure 7 Variation of contact angles described by the slag on various carbonaceous substrates at 1700°C, as a function of time
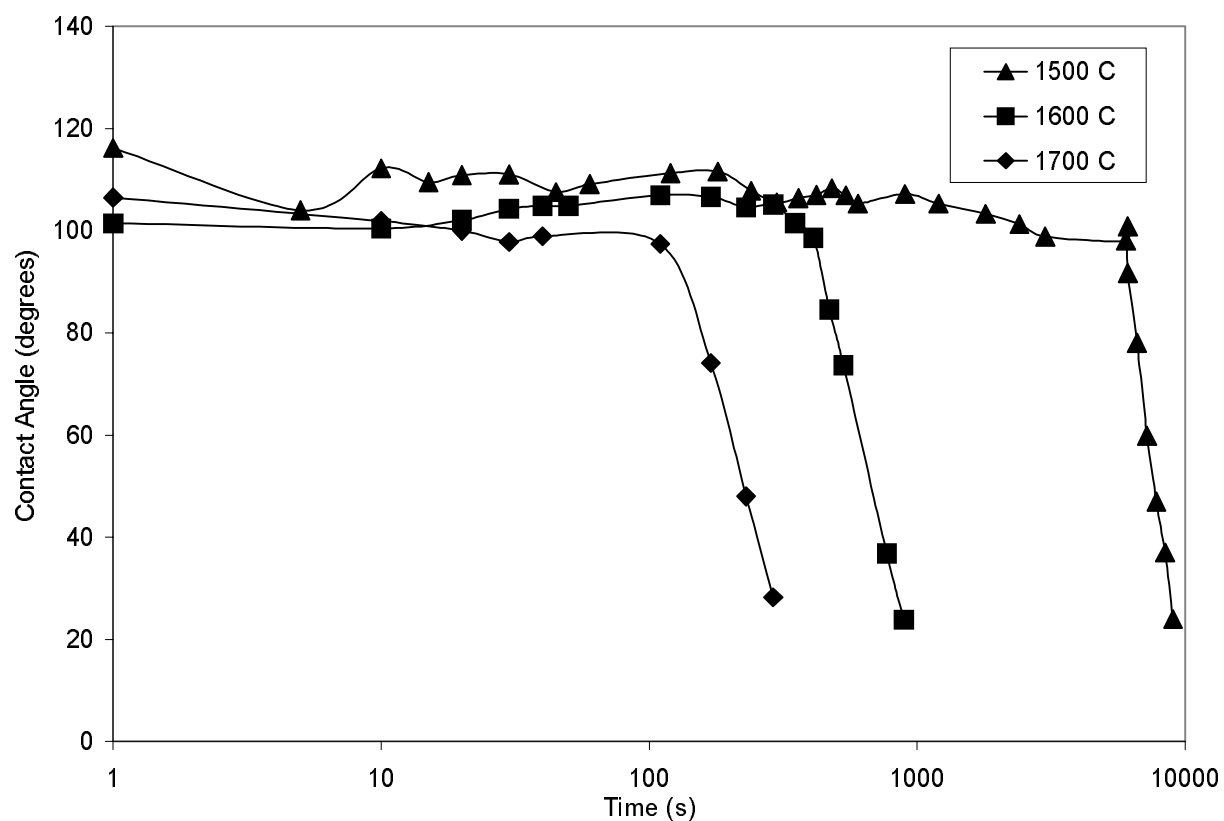
Figure 8 Variation of contact angles described by the slag on Char 1 at 1500℃, 1600℃ and 1700℃, as a function of time
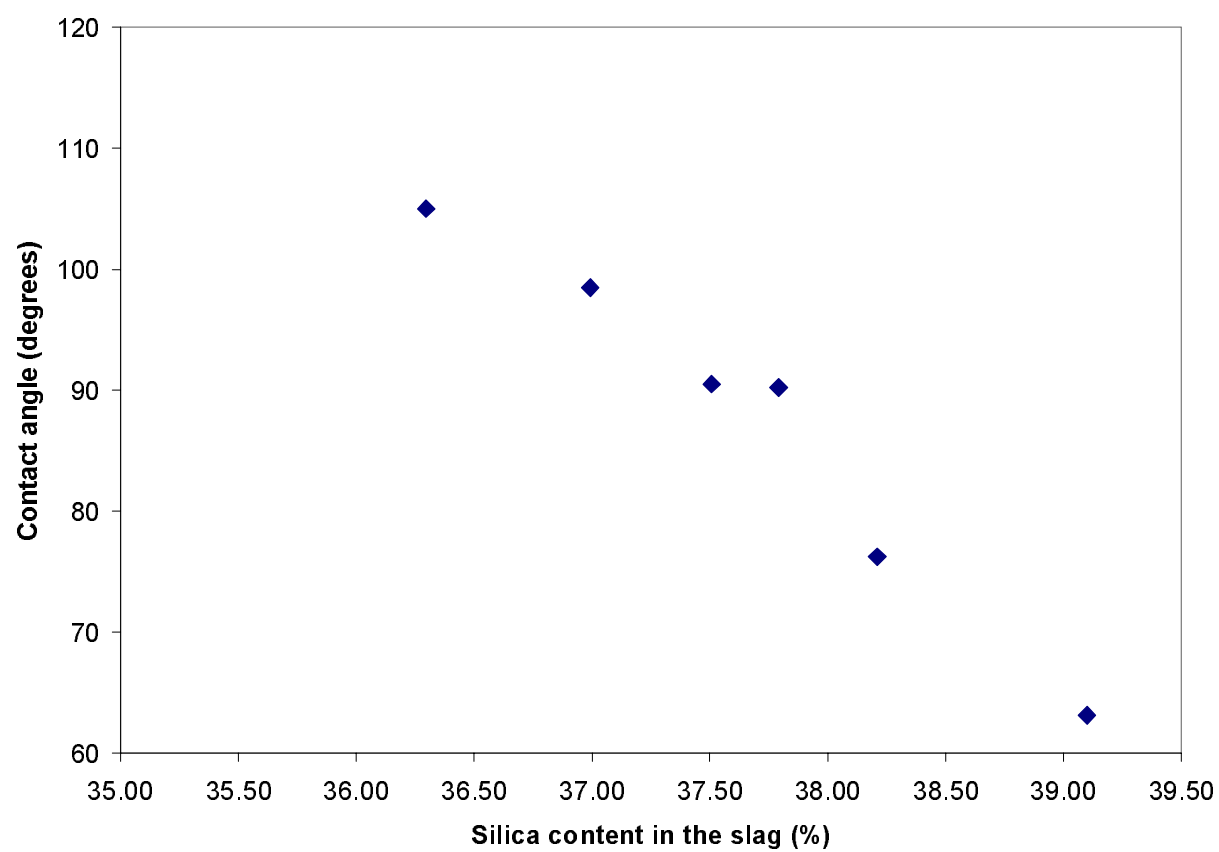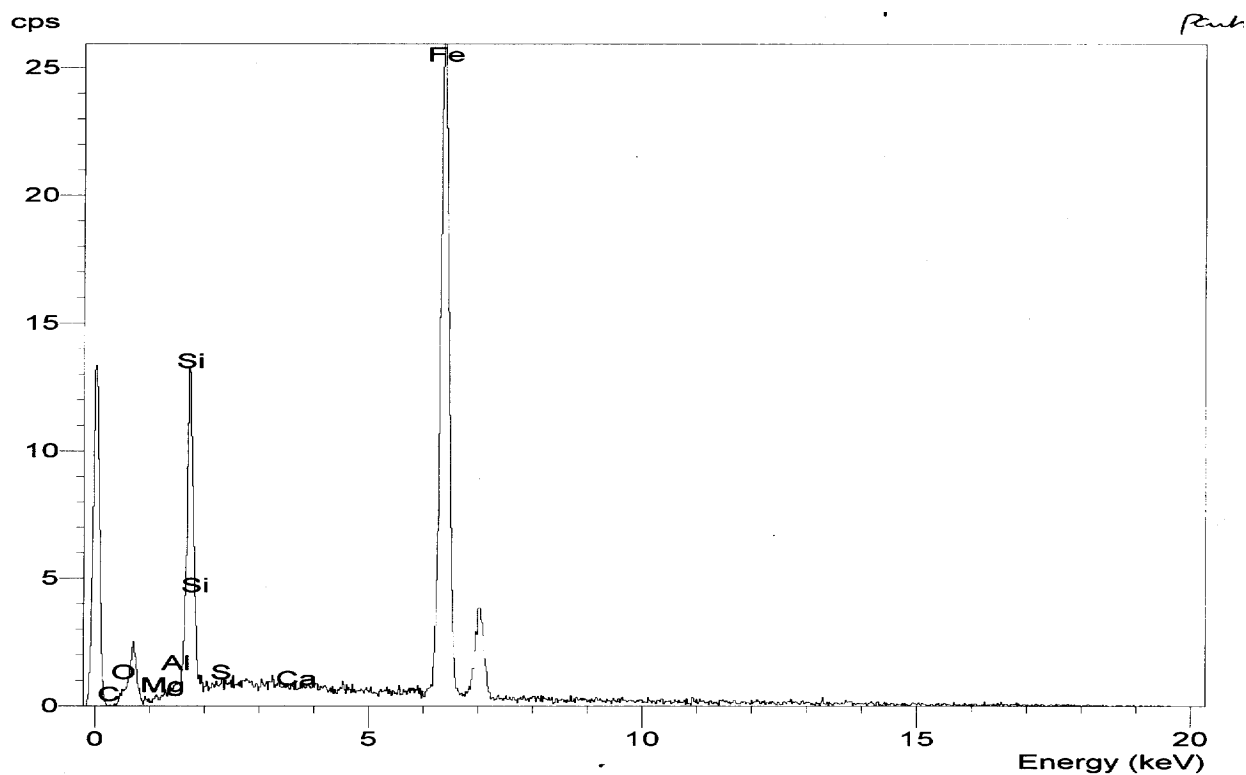

| (a) | (b) |

*Figure 9 High temperature images of the interaction of the slag on Char 1, 11 minutes after melting, at (a) 1500℃, displaying poor wettability, and (b) 1600℃, displaying good wettability*
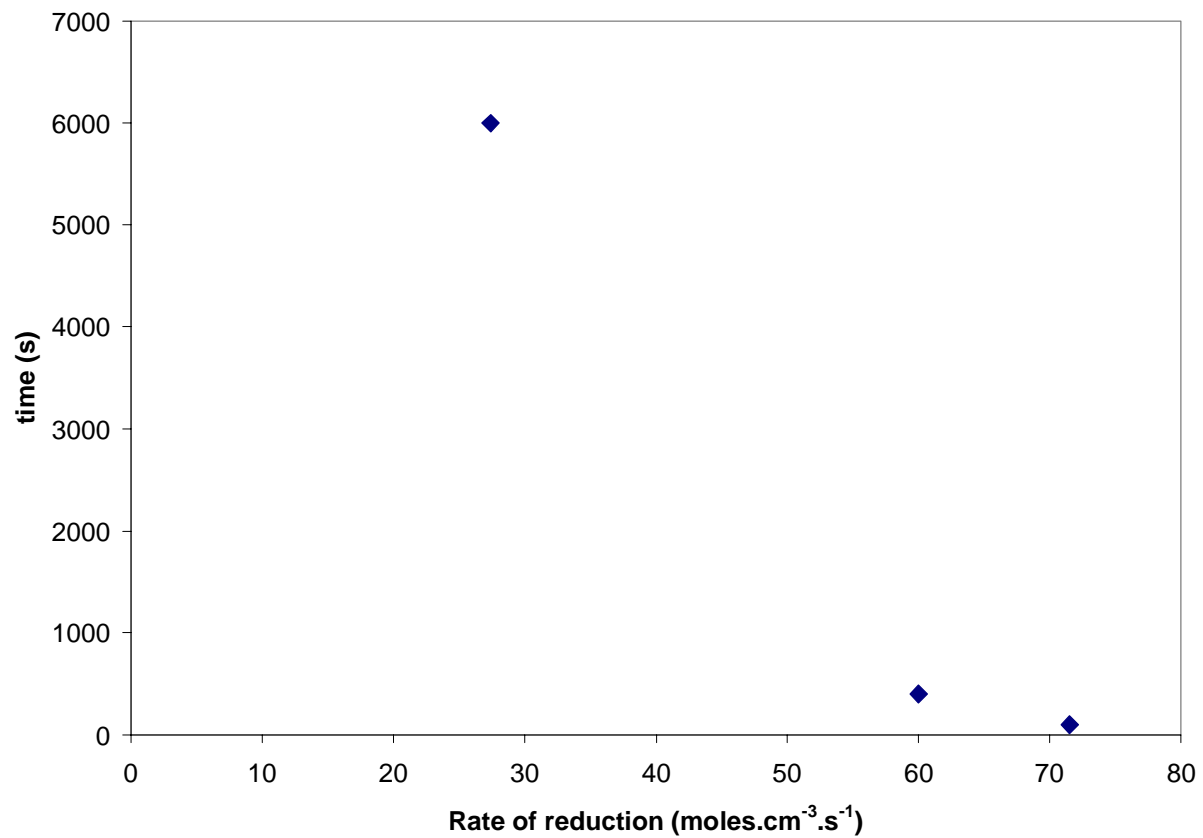
Figure 10 Variation of contact angle as a function of the overall silica content in the modified slag, for different carbonaceous materials, at 1500°C (45 minutes after melting)

Figure 11 X-ray spectrum of the surface of Natural Graphite N, 60 minutes after its interaction with the slag at 1500 °C, indicating presence of Fe and Si rich particles
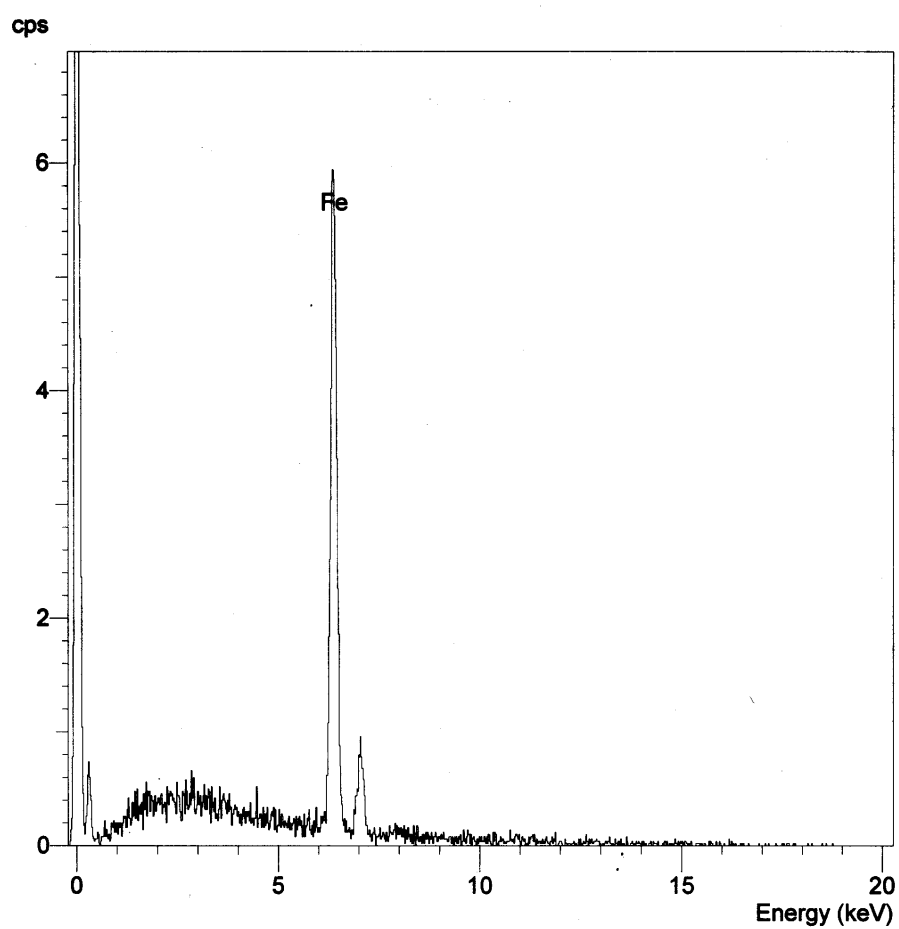
*Figure 12 X-ray spectrum of the surface of Synthetic Graphite S, 60 minutes after its interaction with the slag at 1500 °C, indicating presence of mainly Fe rich particles*

Figure 13 Variation of time required for dynamic changes in contact angle to commence, during the interaction of Char 1 with the slag, as a function of the rate of silica reduction at the three temperatures of 1500℃, 1600℃ and 1700℃
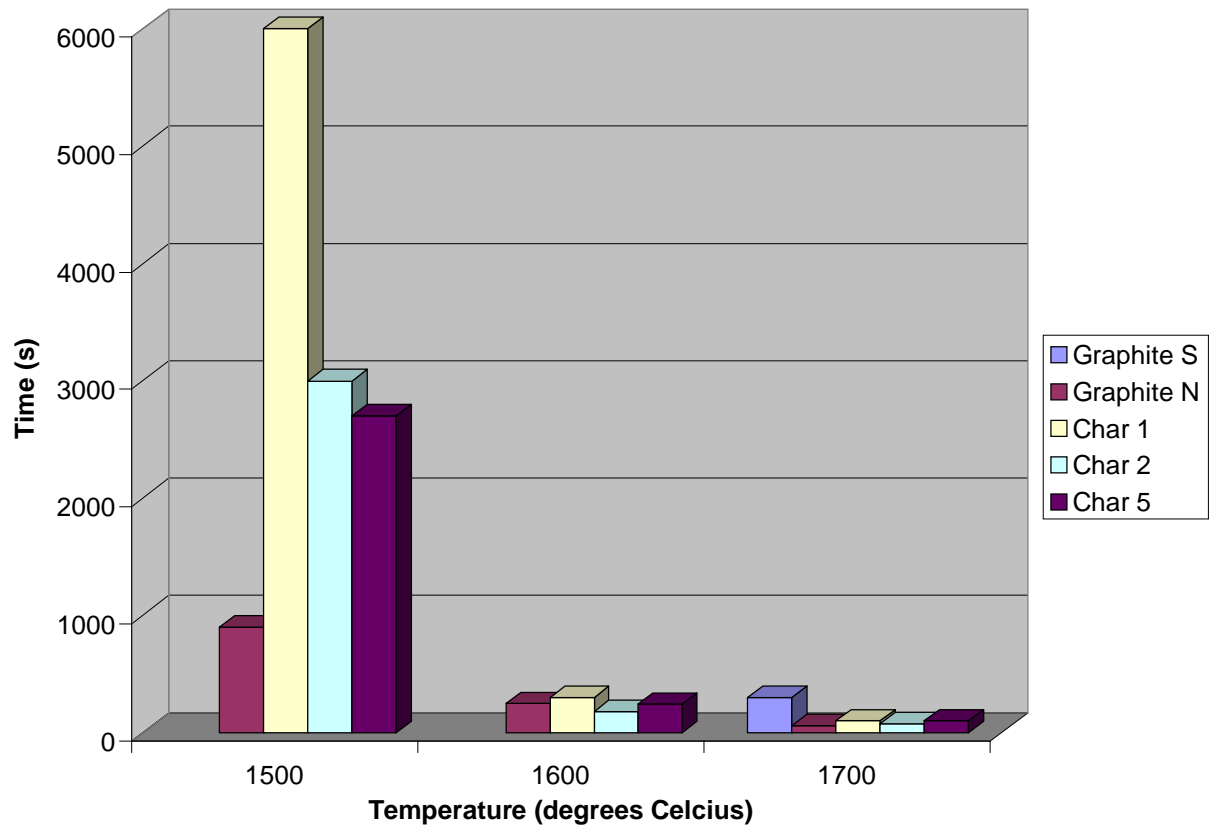
Figure 14 Comparison of the time required for dynamic changes in contact angle to commence, during the interaction of various carbonaceous materials with the slag, at different temperatures

Table 1 *Composition of the various carbonaceous materials used in the study*

	Graphite S	Graphite N	Char 1	Char 2	Char 3	Char 4	Char 5
Carbon (%)	NM	NM	84.58	79.58	NM	87.40	82.25
Hydrogen (%)	NM	NM	0.88	0.66	NM	0.32	0.06
Total Sulphur (%)	NM	0.70	0.36	0.31	0.50	0.32	0.41
Ash (%)	0.01	11.70	9.62	15.42	13.80	9.43	15.15
Mineral Matter (%)	NM	12.00	10.06	16.21	NM	9.98	15.94
Volatile Matter (%)	NM	NM	4.91	5.99	NM	1.74	1.75
Moisture (%)	NM	NM	4.25	5.33	NM	1.83	4.08
Nitrogen (%)	NM	NM	1.42	1.28	NM	1.15	1.25

NM – Not measured

Table 2 *Ash composition and their contents in the carbonaceous materials used in the study*

	Ash Composition (%)							Content in the Carbonaceous Material (%)						
	Graphite S	Graphite N	Char 1	Char 2	Char 3	Char 4	Char 5	Graphite S	Graphite N	Char 1	Char 2	Char 3	Char 4	Char 5
SiO_2	NM	69.00	46.00	47.30	55.50	44.40	50.10	NM	8.07	4.43	7.29	7.66	4.19	7.59
Fe_2O_3	NM	15.00	9.10	10.23	5.80	6.54	15.00	NM	1.76	0.88	1.58	0.80	0.62	2.27
CaO	NM	2.50	2.58	4.33	2.80	1.88	3.22	NM	0.29	0.25	0.67	0.39	0.18	0.49
MgO	NM	0.80	1.01	1.05	0.79	0.38	1.20	NM	0.09	0.10	0.16	0.11	0.04	0.18
Al_2O_3	NM	10.00	36.60	29.90	28.30	40.50	24.20	NM	1.17	3.52	4.61	3.91	3.82	3.67
Alkali	NM	NM	0.53	1.53	1.44	2.22	1.94	NM	NM	0.05	0.24	0.20	0.21	0.29
TiO_2	NM	NM	1.91	1.61	1.60	2.02	1.21	NM	NM	0.18	0.25	0.22	0.19	0.18
SO_3	NM	NM	0.41	2.06	0.59	0.23	0.58	NM	NM	0.04	0.32	0.08	0.02	0.09
P_2O_5	NM	NM	1.61	1.52	1.34	0.88	1.80	NM	NM	0.15	0.23	0.18	0.08	0.27
BaO	NM	NM	0.02	0.04	NM	0.11	0.08	NM	NM	0.00	0.01	NM	0.01	0.01

NM – Not measured

Table 3 *Slag composition used in the study*

Slag Sl. No.	Composition (%)					Simple Basicity
	CaO	SiO$_2$	MgO	Al$_2$O$_3$	Fe$_2$O$_3$	
1	44.40	36.30	6.01	15.60	0.26	1.22

Table 4 *Initial and final composition of the slag droplet during interaction with different carbonaceous materials at 1500°C after 60 minutes [14]*

Component	Initial Composition (%)	Final Composition (%)			
		Graphite S	Char 1	Char 2	Graphite N
MgO	5.10	4.80	4.00	0.20	1.00
Al2O3	15.20	15.30	15.10	17.40	14.00
CaO	43.40	43.50	44.60	47.30	45.00
SiO2	36.00	36.20	35.90	32.00	30.00
Fe2O3	0.30	0.20	0.20	0.00	0.00
SO3	0.00	0.00	2.00	3.20	9.00

Table 5 *Surface tension values of the slag at different temperatures*

Slag No.	Surface Tension (ergs/cm^2)		
	1500°C	1600°C	1700°C
1	480	390	210

NM - not measured