The Influence of Ash Impurities on Interfacial Reactions between Carbonaceous Materials and EAF Slag at 1 550°C

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Carbon/slag interactions have been investigated between two carbonaceous materials, metallurgical coke (18.3 % ash) and natural graphite (2.1 % ash), and an EAF slag (34.8 % Fe2O3) using a sessile drop arrangement at 1 550°C to determine the role played by carbonaceous materials in carbon/slag interactions and interfacial phenomena. Gaseous emissions from metallurgical coke in the presence of slag were much higher than those from coke alone indicating significant carbon/slag interactions with the system exhibiting extensive/rapid iron oxide reduction, very high rates of gas generation but poor gas entrapment within the slag phase. High levels of gas generation led to a strong likelihood of convective transport of reactants and products across the metallurgical coke/slag interface with oxides present in coke ash partially dissolving in molten slag and modifying slag composition. Natural graphite on the other hand showed slow rates of gas generation, slow reduction of iron oxide and excellent gas entrapment. Gases generated from graphite alone were comparable to those generated in the presence of slag and were an order of magnitude lower than the corresponding emissions from metallurgical coke/slag system. Slag interactions with metallurgical coke resulted in lower surface tension due to pickup of silica from coke ash and small droplet volumes; slag interactions with natural graphite gave rise to minor changes in slag properties due to low ash levels and increases in droplet volumes. The rate of gas generation was found to be an important parameter in carbon/slag interactions and needs to be maintained at optimum levels for sustaining gas entrapment within slag over extended periods. This study highlights significant differences in the carbon/slag interactions of two carbonaceous materials with an EAF slag, and the important role played by ash impurities.

KEY WORDS: carbonaceous materials; carbon/slag interactions; interfacial phenomena; EAF steelmaking.

1. Introduction

Worldwide around 40% of steel is produced in small to medium size steel mills based on electric arc furnace scrap melting.1,2) As compared to the integrated steel production route, EAF steelmaking has special advantages of lower capital and operating costs, flexibility of raw materials (use of scrap), flexible feeding materials, higher production rate, higher control of steel making process, higher heat efficiency etc.3) While electricity is the primary energy source for these mills, a significant amount of carbonaceous materials is used as a slag foaming injectant and for recarburising liquid steel; the amount of metallurgical coke injected in electric arc furnaces varies depending on melt shops practice and equipment, generally ranging between 10–20 kg/tonne of steel produced. The operating efficiency of EAF steelmaking is dictated to a certain extent by carbon/slag reactions, associated evolution of gases, slag foaming and metal yield.4) Foamy slag envelops the hot electrodes and arcs and protects the furnace roof and sidewalls from excessive heating and radiation; it provides an insulating layer to the melt, thereby reducing the loss of energy. Mostly, adequate slag foaming occurs at the beginning of refining but decreases towards the end of the heat.

Slag foaming is the result of CO gas generated in the slag layer due to carbon reactions with slag phase; the process depends on factors/processes such as slag/carbon interactions, the rate of gas generation, appropriate slag characteristics for holding and sustaining gas bubbles in the slag layer etc.5–10) Slag foaming has predominantly been studied under steady state conditions with slag chemistry and inert gas flow remaining constant throughout. Foaming was generally found to improve with decreasing surface tension, increasing viscosity of slag and an increased suspension of second phase particles. Addition of sulphur suppressed slag foaming to a small extent and tended to increase the size of CO gas bubbles.11,12) An increase in silica concentration, known to lower the surface tension of slag, led to smaller CO gas bubbles and their easier escape from the slag.13)

The injection of oxygen and carbonaceous materials in industrial EAF furnaces, however create highly dynamic and non-steady state conditions. Kapilashrami et al.14) have shown that dynamic systems display a more complex behaviour than systems under steady state, with foam showing a fluctuating behaviour with time. Oxidation and reduc-
tion reactions continuously change slag composition; chemical reactions producing CO gas are also likely to change significantly with time. Morales et al.\(^{15}\) have developed the concept of a dynamic foaming index based on the rate of gas generation and the rate of change of slag volume. While a number of studies have been reported on the influence of slag chemistry and characteristics on slag foaming, there is very limited understanding on the role played by carbonaceous materials and the influence of their fundamental characteristics (e.g. structural order, ash content and composition etc.) on the rate of gas generation, interfacial phenomena, and slag foaming. The present study investigates the influence of carbonaceous materials on carbon/slag interactions and foaming behaviour with a specific focus on the rate of gas generation, interfacial phenomena and the capacity of slag to trap gas.

In this article, we report in-depth sessile drop investigations (1550°C) on two carbonaceous materials (metallurgical coke and natural graphite) and an EAF slag (34.8%) with an aim to develop a fundamental understanding of carbon/slag interactions during EAF steelmaking. Along with a quantitative estimation of changes in slag volume as a function of time, we report results on off gas generation (CO, CO\(_2\)), optical/electron microscopic investigations on the interfacial region, followed by a critical analysis of interfacial phenomena, gas entrapment by the slag and implications for slag foaming.

### 2. Experimental

#### 2.1. Material Characteristics

Two carbonaceous materials, metallurgical coke and natural graphite, were used in this investigation; proximate and ash analysis for these materials are given in Tables 1 and 2 respectively. The chemical composition of slag is given in Table 3. While natural graphite had a highly ordered crystalline structure (Lc = 260 Å), metallurgical coke had a low structural order (Lc = 24 Å) as determined from the width of (002) peak using Scherrer equation.\(^{16}\) Carbonaceous substrates were prepared by grinding powdered carbons finely (<60 μm) and compacting without a binder in a steel die using a hydraulic press and pressing to a pressure of 7.75 MPa. The compacted, cylindrical substrate of diameter 20 mm and thickness 3–4 mm was then removed from the die and placed on the alumina stage of the sessile-drop experimental assembly.

| Table 1. Chemical compositions (wt%) of carbonaceous materials. |
|-----------------|-----------------|-----------------|
| Composition     | Metallurgical Coke | Natural Graphite |
| Carbon          | 78.7             | 97.6            |
| Volatiles       | 3.0              | 0.3             |
| Ash             | 18.30            | 2.1             |
| Sulphur         | 0.32             | 0.05            |
| Moisture        | 1.3              | 0.3             |
| Surface area (m\(^2\)/g) | 7.2197          | 2.8233          |

| Table 2. Ash analysis (wt%). |
|-----------------|-----------------|
| Components      | Metallurgical Coke | Natural Graphite |
| SiO\(_2\)       | 50.70           | 42.60           |
| Al\(_2\)O\(_3\)  | 36.0            | 16.40           |
| FeO\(_3\)       | 4.8             | 17.60           |
| TiO\(_2\)       | 1.40            | 0.63            |
| CaO             | 3.30            | 8.90            |
| MgO             | 0.94            | 10.50           |
| Na\(_2\)O       | 0.39            | 1.40            |
| K\(_2\)O        | 0.53            | 1.80            |
| P\(_2\)O\(_5\)   | 1.60            | 0.12            |
| Mn\(_2\)O\(_4\)  | 0.64            | 0.21            |
| SO\(_3\)        | 0.39            | 0.07            |

| Table 3. The chemical composition of slag (wt%). |
|-----------------|-------------|
|                  | CaO         |
|                  | 29.6        |
|                  | FeO\(_3\)   | 34.8        |
|                  | Al\(_2\)O\(_3\) | 8.4        |
|                  | MgO         | 9.4         |
|                  | SiO\(_2\)   | 13          |
|                  | MnO         | 5.7         |

### 2.2. Carbon/Slag Interactions

Sessile drop investigations on the carbon/slag system were carried out at 1550°C in a laboratory scale, horizontal tube resistance furnace.\(^{17}\) This technique can be used to continuously monitor the changes in droplet volume (a measure of gas entrapment) as function of time.\(^{18}\) A schematic diagram of the experimental set up is shown in Fig. 1. Initially, the sample was held on a specimen holder, which could be pushed to the centre of the hot zone in the furnace with the help of a stainless steel rod. The assembly was held in the cold zone of the furnace until the desired temperature (1550°C) was attained and was then inserted into the hot zone. This eliminated any reaction that could occur at lower temperatures and possibly influence the phe-

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nomina to be studied at the temperature of interest. The continuous/or sporadic evolution of gases, either from in-situ reactions within the carbonaceous substrate or from chemical reactions between the substrate and the slag droplet, caused the slag droplet to move around on the substrate. The weight of the slag used was \( \sim 0.065 \) g; a few experiments were also carried out with a slag weight of \( 0.032 \) g. Heavier slag droplets had a high tendency to roll off the substrate. The furnace tube was purged with argon throughout the duration of the experiment with a flow rate of \( 1.0 \) L/min. The volumes of CO and CO\(_2\) evolving from the reaction assembly were measured continuously through an on-line off-gas analyser. In general, there was a time delay of 40 to 60 s before the evolution of gases was recorded by the mass spectrometer. The gas data was used to determine the overall reaction rates, and number of moles of carbon and oxygen removed from the reacting assembly as a function of time.

The melting of slag marked the beginning of the contact time. A 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 CCD camera was channelled to a digital video recorder (DVD) and a television monitor to record the entire experimental process as a function of time. This feature allows specific images, displaying the contact between the slag and carbonaceous material to be captured as a function of time from the DVD, which were subsequently processed by a computer. A time-date generator was used in the system to display the duration of the experimental process. Detailed image analysis techniques are available in the literature for an accurate determination of contact angles and surface tension from the shape of sessile drops. Maze and Burnet\(^{19}\) have developed a numerical algorithm using a non-linear regression analysis for computing the droplet profile from a number of arbitrarily selected co-ordinates on the experimentally measured sessile drop. However in a reactive system, a detailed mathematical drop-shape analysis will be extremely difficult due to continuous/sporadic evolution of gases and dynamic changes in the droplet shape and size. In most of the images, small deformities in the bubble outline caused by the presence of gas bubbles just below the surface prior to bubble rupture and gaseous escape could clearly be observed. As the droplet is not able to reach an equilibrium configuration, fitting a mathematically computed profile to the observed droplet through detailed image analysis is not likely to yield valuable/reliable information. Sessile-drop arrangement is used extensively to measure contact angles at the solid/liquid interface, high levels of gas generation across the interface significantly affected the accuracy of our contact angle measurements. Although contact angles were measured in the present study, results have not reported due to their limited accuracy.

Dynamic changes in the droplet volume and contact area were determined from the captured images with the help of especially designed data processing software. Data processing was carried out in two stages: the first stage involved an initial transformation of digital video/audio signals into “.mpeg2” code followed by their transformation into individual bit map frames (“.bmp” code). As a one hour video translates to 90,000 frames, a ‘Linux’ based program was developed to select specific frames out of the experimental data for further processing. The second stage of data processing involved the computation of slag droplet volume in a chosen frame. As the primary focus of this work was on a quantitative estimation of gas entrapment and rapidly changing droplet volumes, the slag droplet on the substrate was assumed to have a truncated spherical shape. In a semi-automatic procedure, a circular marquee was fitted manually to provide a best fit to the slag droplet, with the user playing an important role in identifying the optimum spherical shape for the slag droplet at a given instant of time. The volume of the slag droplet and area of contact between slag and substrate were computed in terms of the radius ‘\( r \)’ of the droplet and the truncated height ‘\( h \)’ (Fig. 2). The volume ‘\( V \)’ of the segmented sphere is given by

\[
V = \frac{\pi}{3} (4r^3 - h^2(3h - h))
\] ............................(1)

The area of contact ‘\( A \)’ between the slag droplet and the substrate, is given by

\[
A = \pi h(2r - h)
\] ............................(2)

The data from all images was stored in a data file for further processing. Minor deviations from the spherical outline were not explicitly taken into account and were neglected (estimated error \( \sim <5\% \)). Further details are given elsewhere.\(^{19}\) While it is difficult to measure the absolute volume of the droplet in the absence of a reference marker, sessile-drop slag foaming software generates volume ratio “\( V/V_0 \)” and area ratio “\( A/A_0 \)” as a function of time, where \( V_0 \) and \( A_0 \) are respectively the initial volume and contact area for the slag droplet. A very large number (>1000) of video images were analysed to determine droplet volumes and areas of contact as a function of time.

2.3. Interfacial Phenomena

Optical microscopic and FESEM studies were carried out on the interfacial region of quenched carbon/slag assemblies. Once the sample was pushed in the hot zone and the counter started after the melting of the slag droplet, the reaction time was closely monitored. The slag droplet and the carbon substrate were quenched by withdrawing the tray into the cold zone of the furnace after fixed periods of time. Samples were produced for the following times: 1, 2, 4, 8,
15, 20 min. For microscopic investigations, the carbon/slag assembly was set in an epoxy resin mould; the set assembly was then sectioned carefully to expose vertical cross-section of the carbon substrate/slag assembly and was again reset in a mould. After the final polishing was completed, the samples were dried on a baking oven at 60°C for 12 h to remove moisture, if any, from the samples. These were then used to investigate the generation of metal droplets as a result of iron oxide reduction and distribution of gas bubbles trapped within the slag droplet. Electron microscopic investigations were also carried out on cross-sections of the slag droplet using a Field Emission Scanning Electron Microscope (FESEM) and analysed with Energy Dispersive Spectroscopy (EDS) to determine the time-dependent growth of reaction products.

3. Results

3.1. Off-gas (CO, CO₂) Generation

The off-gas generation data as measured using on-line IR gas analyser is shown in Figs. 3 and 4. Figure 3 shows the cumulative volume of gases emitted (CO, CO₂) from a blank natural graphite substrate as well as from the natural graphite/slag assembly. The numbers of moles of carbon and oxygen removed from the reacting assembly have also been shown in the figure. The volumes of CO/CO₂ detected in off-gases were comparable in two cases. The overall CO level was almost double of CO₂ emitted. The corresponding results for metallurgical coke are given in Fig. 4. Volatile matter present in both materials is expected to be released in the cold zone of the furnace and is unlikely to have much influence on the results presented. The off-gas results for metallurgical coke were significantly different from natural graphite; both CO and CO₂ levels were an order of magnitude higher under similar experimental conditions. After 1500 s in the hot zone at 1550°C, the cumulative volume of CO gas emitted from the blank substrate of metallurgical coke was seven times higher than from natural graphite, with CO₂ levels from metallurgical coke being 1.5 times higher. In the presence of slag, CO gas emitted from metallurgical coke was nearly 12 times higher than the corresponding result from natural graphite, indicating a significant level of carbon/slag interaction. The amount of carbon removed from metallurgical coke was nearly 10 times the carbon removed from natural graphite. The rate of gas generation (CO+CO₂) from both carbonaceous substrates in the presence of slag is shown in Fig. 5 and showed a significant variation with time.
3.2. Carbon/Slag Interactions

All experimental runs were recorded up to 30 min. A few representative video images of the slag droplet with metallurgical coke and natural graphite are shown in Fig. 6 as a function of time. The size of the slag droplet in contact with metallurgical coke did not show a significant variation with time during initial stages. The slag droplet also did not show much movement with time, and was reasonably spherical in shape. Although not quite captured on the static images shown in Fig. 6, the slag droplet showed small but continuous fluctuations in size associated with the generation and subsequent release of gas. For natural graphite substrate, the size of the slag droplet increased significantly with time as compared to initial size. Due to a continuous/sporadic evolution of CO gas bubbles within the slag droplet, the droplet showed minor deviations from a spherical shape. Images were analysed every 5 s during the initial stages of contact and every 30 s during later periods.

The computed results on V/V_o and A/A_o for natural graphite and metallurgical coke have been plotted in Fig. 7 as a function of time. During 10 min of contact, the volume ratio V/V_o from metallurgical coke decreased from 1.0 to 0.5 indicating a significant reduction of FeO decreasing the initial volume of slag and also a lower extent of gas entrapment by the slag. This decrease however was not smooth; fluctuating volume ratio values ranging from 0.2 to 2.0 were observed at certain times indicating generation and subsequent release of gas. The estimated values of contact area ratio A/A_o, were found to fluctuate around 1.0 during this period. Natural graphite however showed significantly different trends with much higher levels of droplet volumes. The volume ratio V/V_o showed large fluctuations, with the drop growing up to seven times larger in size due to the gas trapped within the slag and then dropping down to a much smaller size with the release of gas. This trend continued several times during first 5 min; volume ratio eventually settled down to 0.5 after 10 min of contact. This indicates that the decrease in slag volume took much longer in case of natural graphite as compared to metallurgical coke, suggesting slow reduction of FeO over extended periods. The contact area ratio A/A_o reached a maximum of 3.5 during initial contact and reduced to 1.25 with time. Large fluctuations in volume and area ratios point towards significant levels of gases trapped and subsequently released during carbon/slاغ interactions.

3.3. Interfacial Phenomena

Optical microscopic images of metallurgical coke/slاغ assembles are presented in Fig. 8. These results are on quenched reaction assemblies after being exposed to high temperatures for fixed periods of time. Extensive reduction of iron oxide was observed after 1 min of contact. While a large number of molten iron droplets of varying sizes could be seen suspended in the slag droplet, chunks of reduced iron were also observed on the substrate. Gas bubbles trapped within the slag droplet were generally quite small in size, except for one large bubble. After 4 min of contact, the region of slag droplet containing reduced iron droplets had shrunk considerably; a large chunk of reduced iron was seen precipitated on the substrate. A FESEM/EDS image on the dark region of the slag droplet after 15 min in the hot zone is shown in Fig. 9(a). Predominant components in this region were CaO, MgO, SiO_2 with very small levels of molten iron being observed. A FESEM/EDS image (Fig. 9(b)) on the bright region of the slag droplet showed local regions of molten iron superimposed on other slag oxides.
Optical microscopic images of natural graphite/slag assemblies are presented in Fig. 10; these are significantly different from metallurgical coke. A key feature of natural graphite substrate was the generation of gases which enveloped the reaction assembly during initial stages (Fig. 6). In the optical microscope image after 1 minute, large quantity of gas was observed in the region just above the slag droplet along with a number of gas bubbles trapped (dark regions).

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As compared to metallurgical coke, iron oxide reduction appeared to be much reduced with molten iron droplets present closer to the outer edge of slag droplet rather than in regions closer to the carbonaceous substrate. A FESEM/EDS on natural graphite/slag system (Fig. 11) showed that the lower region of the slag droplet was completely depleted of iron after 15 min of contact.

Optical microscopic images of natural graphite/slag assemblies are presented in Fig. 10; these are significantly different from metallurgical coke. A key feature of natural graphite substrate was the generation of gases which enveloped the reaction assembly during initial stages (Fig. 6). In the optical microscope image after 1 minute, large quantity of gas was observed in the region just above the graphite substrate, well trapped by the slag droplet. This gas, which could have been generated in-situ within the graphite substrate or from interactions of carbon with slag, significantly reduced the direct contact between the carbonaceous substrate and slag. This effect was significant for contacts up to four minutes, reducing slowly thereafter. As compared to metallurgical coke, iron oxide reduction appeared to be much reduced with molten iron droplets present closer to the outer edge of slag droplet rather than in regions closer to the carbonaceous substrate. A FESEM/EDS on natural graphite/slag system (Fig. 11) showed that the lower region of the slag droplet was completely depleted of iron after 15 min of contact.
4. Discussion

Significant differences were observed in the interactions of natural graphite and metallurgical coke with an iron oxide rich (34.8 wt%) EAF slag. Gaseous emissions from metallurgical coke were an order of magnitude higher than the corresponding emissions from natural graphite (Figs. 3 and 4). High levels of off-gases (CO, CO₂) were emitted from the blank metallurgical coke substrate; CO₂ levels were relatively much lower. These emissions from the blank substrate indicate _in-situ_ reduction of ash oxides, and coke gasification via reactions with CO₂ (CO₂ + C = 2CO). In the presence of slag, while there was a significant increase in CO emissions, CO₂ levels decreased further to less than 3%. In his study on the reduction of Fe₂O₃ and FeO by a range of carbonaceous materials in the temperature range 900°C to 1200°C, Fruehan showed that CO₂/CO ratio dropped significantly during reduction from 0.55 at 900°C to 0.13 at 1200°C, with the ratio averaging around 0.13 during the final 20% of the reaction. Kohl and Marineck obtained a CO₂/CO ratio of 0.25 in the early stages of the reaction and about 0.1 in the final stages. With metallurgical coke, the CO₂/CO ratio from the reaction assembly approached 0.03 within 300 s; optical microscopic images after few minutes of contact (Fig. 8) also showed extensive reduction of iron oxide in slag.

Natural graphite on the other hand showed much lower levels of CO and CO₂ emissions. The primary source of this gas is through reduction of iron oxide in slag by the CO at the gas–slag interface giving liquid iron and CO₂ as products. Optical microscopic images also reflected this behaviour during initial stages of contact (Fig. 10). After 1 min, a large gaseous region was seen trapped within the substrate and the slag droplet along with several much smaller gas bubbles within the slag droplet. The cumulative volume of CO gas from the blank substrate was marginally higher than in the presence of slag indicating that some of the gas produced by the substrate and through carbon/slag interactions was trapped within the slag and was therefore not detected in off-gases. The CO₂/CO ratio for natural graphite was quite high (>0.3) indicating that reduction of iron oxide occurs indirectly through CO gas resulting in the formation of CO₂. The gasification of graphite with CO₂ is also expected to be slower than coke.

Figure 5 reflects the rates of chemical reactions producing gas (e.g., reduction of iron oxide, coke gasification) and their variation with the progress of reactions. As expected, the rate was much higher for metallurgical coke as compared to natural graphite. Higher surface area values will also support much higher reactivity for metallurgical coke as compared to natural graphite (Table 1). The rate of gas generation in both cases showed a sharp increase with time, peaking shortly thereafter followed by a rapid decrease. After 500 s, both curves had nearly flattened out with marginal decreases in gas generation over longer periods indicating a slowing down and a near completion of reduction reactions.

Despite high levels of gases produced, metallurgical coke substrate did not show much gas entrapment (Figs. 6 and 7). The volume ratio (V/V₀) for metallurgical coke was seen to decrease from 1.0 to 0.5 after 10 min. A number of gas bubbles were generally seen trapped within the slag droplet; these were small in size except for a few large ones. Teasdale and Hayes have used a gas ferrying mechanism, wherein CO gas produced in the initial reaction between carbon and slag gets transported through the gas phase and reacts with FeO in slag to produce CO₂ and metallic iron. This CO₂ is ferried back to carbon, where gasification of CO₂ to CO takes place via the Boudard reaction. The cycle of reactions is then repeated several times. Carbon from the substrate can also dissolve into reduced molten iron with solute carbon further participating in reduction reactions. Due to high levels of gas generation, there is therefore a strong likelihood of convective transport of reactants and products across the metallurgical coke/slag interface with oxides present in coke ash partially dissolving in molten slag and modifying slag composition. It is well known that silica is a very surface-active component in steelmaking slags; an increase in silica concentration will lower the surface tension of slag. Silica was a major impurity oxide (50.7%) present in coke ash (18.3%), and its diffusion from the substrate into slag will lead to a lowering of surface tension of the slag. A reduced surface tension of slag will favour a reduction in the size of gas bubbles and also impair its ability to hold gas. Alumina was another significant impurity oxide (36.0 wt%) present in coke ash. According to atomistic simulations of Khanna and Sahajwalla, poor wetting between alumina and molten iron results in a strong tendency between alumina and liquid iron to be mutually exclusive from their immediate neighbourhood. Due to the presence of large amount of reduced metal in the close proximity of the coke substrate, there is not much likelihood of alumina dissolving in to slag. Due to extensive reduction of iron oxide, its levels in slag will be lowered. According to slag phase diagrams, a lower iron oxide content will increase the melting point of slag; which will inturn reduce its liquid fraction and enhance the viscosity of the slag. Chemical and other interactions between metallurgical coke and EAF slag will result in SiO₂ from ash to increase silica levels in slag lowering surface tension and making it easier for gases to escape.

In the case of natural graphite, the tendency of slag droplet to hold gas within resulted in a significant increase in the volume of the slag droplet (Fig. 6). This led to the droplet volume ratio fluctuating widely due to gas hold-up and subsequent release (Fig. 7). This behaviour was observed during initial 5 min, with system settling down later on. During initial stages (up to 4 min), there was limited direct contact between the slag and natural graphite substrate. While a small amount of reduced iron could be seen on the substrate (Fig. 10; 1 min), a large number of small droplets of reduced iron were observed in the outer regions of the slag droplet. Relatively high level of CO₂ (Fig. 4) in the off-gases (>30%), supports indirect reduction being the dominant mechanism for natural graphite. Sasaki and Soma have pointed out that when CO₂ in generating gas exists more than 10%, direct reduction is not significant but indirect reduction is the dominant mechanism. Indirect reduction of iron-oxide takes place at the gas–slag interface by the CO gas trapped within and by the gas surrounding the slag droplet. Due to limited area of contact and gases trapped at the carbon/slag interface, there is little opportu-
nity for ash components in natural graphite to diffuse into slag. With increasing times however, the size of gaseous region trapped at the interface reduces leading to an increased contact between the substrate thereby enhancing the transfer of ash components into slag. After 15 min, lower regions of the slag droplet were depleted of iron oxide (Fig. 11). Interactions of natural graphite with slag gave rise to minor changes in viscosity and surface tension and large bubble sizes.

The key difference between the two cases is the 2% and 18% of ash. Slag is expected to have a better wetting with ash oxides than with carbon. With 18% ash present in metallurgical coke, the ash particles can form a 2-D interconnected network along the surface. The CO bubbles, formed originally along the carbon/slag interface, will prefer to grow vertically due to high contact angle with ash particles, leading to their separation with a relatively small volume. The surface then gets cleaned for further reactions and further bubbles, and reaction is not slowed down by the bubbles. On the other hand, in the case of graphite the bubbles grow with low contact angle, almost covering the whole carbon surface as 2% ash is not able to form any kind of 2-D surface network. As a result, the bubble separates only at very large volumes, and reduces the reaction rate considerably. These results clearly bring out the influence of ash and significant differences in carbon/slag interactions for metallurgical coke and natural graphite.

5. Conclusions

(1) High levels of gaseous emissions (CO and CO$_2$) were recorded for metallurgical coke/slag system; these were an order of magnitude higher than the corresponding gases emitted from natural graphite/slag system. For metallurgical coke, gases emitted in the presence of slag were much higher than those from a blank substrate indicating significant carbon/slag interactions. For natural graphite, gases generated from the blank substrate were comparable to those in the presence of slag.

(2) Despite much lower levels of off-gases detected, natural graphite showed extensive gas entrapment with the size of the slag droplet increasing to nearly seven times the initial volume. The size of the droplet showed wide fluctuations with time and was associated with trapping and subsequent release of gases. The contact area also increased to three times the initial area eventually settling down after 10 min. Metallurgical coke did not show much gas entrapment with droplet volume reducing to nearly half after 10 min; contact area however did not change much as the reduction in droplet size was accompanied by a slightly improved wetting on the substrate.

(3) This in-depth study has clearly brought out the significant role played by the carbonaceous materials and the influence of their fundamental characteristics on various aspects of carbon/slag interactions. The interactions of natural graphite (2.1% ash) and metallurgical coke (18.3% ash) with EAF slag showed major differences in gas generation, carbon/slag interactions and rate of iron oxide reduction.

Metallurgical coke showed extensive/rapid iron oxide reduction, very high rates of gas generation but poor foaming behaviour. Although the diffusion of ash impurities into slag, especially silica, was expected to significantly influence foaming behaviour through lowering of surface tension, large quantities of gas produced in chemical reactions between slag and metallurgical coke could not be contained within the slag and generally escaped the reaction assembly. Natural graphite on the other hand showed excellent slag volumes but slow reduction of iron oxide. Slower rates of gas generation and higher surface tension values made it easier for slag to trap gases and sustain foaming. The rate of gas generation was found to be an important parameter in carbon/slag interactions and needs to be optimised to maintain optimum levels/duration of gas entrapment by the slag and foaming behaviour.

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