1. Introduction

Over the past two decades, the use of EAF for the production of steel has grown dramatically all over the world due to its ability to run on a relatively small scale with low capital costs and energy savings. Its versatility lies in its capability to use various kinds of raw materials. Predominantly 100% steel scrap is melted and converted into high quality steel using chemical energy and electrical energy from the arcing process. Depending on the melt shop operation, about 60–65% counts for electrical energy, while the reminder of 35–40% is obtained from the chemical energy, derived from combustion of natural gas, carbon oxidation and other chemical reactions such as oxidation of iron and silicon.\(^1\)

The combustion of carbon based materials releases chemical energy. However, their effective usage as an energy resource depends on the kinetics of their reaction with oxygen and the extent to which they are converted to CO gas (the chemical reaction that liberates energy). In conventional EAF steelmaking, natural gas is generally used as a supplementary energy source. Looking at the economical aspects and shortage of natural gas, it has become important to consider different carbon sources, which are both energy effective and environmentally friendly. Polymeric materials, such as rubbers, have properties which could meet the specific needs required for these applications. Being composed of long hydrocarbon chains, these materials contain high volatile matter with low ash and moisture content.

Previous research has been conducted, by our group, to investigate the use of rubber as a source of carbon and energy in electric arc furnace (EAF) steelmaking.\(^2,3\) In 2003 the electric arc furnaces in U.S. began to use scrap tyres as a source of carbon and steel for manufacturing high-carbon steel products by introducing whole tires into a charge bucket. Two companies (Nucor Steel-Auburn NY and IPSCO Steel-Mobile AL) began using scrap tyres in the steelmaking process\(^4\) after completing initial trials. The practice of using waste tyres in steelmaking industry initially started in Japan in 1998\(^5\) and continued in France in 2003.\(^6\)

In EAF steelmaking, a foamy slag produces substantial savings such as: decreasing electricity consumption, protecting the equipment, covering the arcs and the refractory lining, as well as reducing the arc noise.\(^7\) Slag foaming involves the expansion of molten slag by CO gas bubbles evolving from chemical reactions at the slag–metal interface. Hence, the phenomenon is influenced by two main factors: 1) rate of gas evolution by the reduction reactions and 2) the stability of the foamy layer in the melt. The latter...
factor is dependent on the bubble size and lamellae stability. On the other hand, viscosity and surface tension influences the movement of the bubbles in the gas dispersed liquid. Foaming was described by Kozakevitch and more recently by Hara et al. in terms of surface chemistry. They measured the foam life and foam height for binary and ternary systems composed of CaO–SiO₂–FeO and correlated the foam height with the physicochemical properties of metallurgical slags.

Foaming is a dynamic phenomenon involving one dimensional two-phase flow. With time foaming shows fluctuating behavior due to the changes occurring in the slag composition. To account for these dynamic conditions Morales et al. attempted to quantify the foaming behavior by introducing a foaming index which is correlated to the changes in the slag volume and the rate of generated gas. Bikerman et al. first described a foaming index which had been empirically related to physical properties of the slag such as the surface tension (σ), viscosity (η), and density (ρ) of the liquid slag and the size of the bubbles (dₘ). This index has a unit of time and can be considered as the residence time of the bubbles in the foam. Foaming has been shown to improve with decreasing surface tension and increasing viscosity of slag, although the magnitude of the influence of these parameters on the changes in the foaming behavior has not been established as yet. On the other hand, presence of sulphur is known to suppress slag foaming to a small extent. Lower surface tension leads to increased size of gas bubbles and decrease stability of the foamy slag. However, this view of the surface activity of sulphur has been disputed by different other researchers.

Along the years, several techniques have been developed to study the slag foaming and gas generation phenomena as a function of slag chemistry. However, limited work has been done to consider the carbon type and its characteristics upon its interactions with the slag.

The present study investigates the influence of metallurgical coke and its blends with rubber on carbon/slag interactions and associated gas generation, interfacial phenomena as well as the ability of slag to trap gases, during slag/carbon interactions at 1 550°C.

Using the sessile drop approach, interfacial reactions taking place in the slag/carbon region were investigated at 1 550°C in a horizontal tube furnace under inert atmosphere of 1 L/min Ar (99.99% purity). Metallurgical coke and its blends with rubber, in different proportions, have been used as carbonaceous materials along with an EAF slag. To qualitatively illustrate the differences between the two blends a bar chart was employed and it is presented in Fig. 1. The

2. Experimental
2.1. Material Characteristics
Metallurgical coke and its blends with rubber, in different concentration, were used as carbonaceous materials in this study and their composition is given in Table 1, while the analyses of the ash content of these two components are presented in Table 2. Waste rubber tyres were cryogenically crushed to a size of <0.5 cm in liquid nitrogen and mixed in weight proportions with metallurgical coke, as the bar chart in Fig. 1 shows.

The blends were further crushed in a jaw crusher and a vibrating grinder to increase the uniformity in particle size distribution. After these processes, particles with sizes ranging between 0.45 and 0.47 mm were obtained. The blends were of 1 200°C to conduct the initial combustion reaction. The residual char collected at the bottom of the furnace tube is further on subjected to carbon/slag investigations. Partial combustion of carbon in coke–rubber blends during passage through DTF resulted in a higher concentration of ash in the carbonaceous residues, while the volatiles still present in the blends are predominantly unburnt hydrocarbons.

The chemical composition of the industrial slag provided

Table 1. Chemical compositions (wt%) of carbonaceous materials.

|                | Proximate and ultimate analysis (wt%) |                |                |
|----------------|---------------------------------------|----------------|----------------|
|                | Metallurgical coke (raw) | 100% Rubber tyre | Blend 1 (after DTF) | Blend 2 (after DTF) |
| Moisture       | 1.30 | 0.9 | 1 | 0.9 |
| Ash            | 18.3 | 5.7 | 27.78 | 22.28 |
| Volatile matter| 3.00 | 6.2 | 5.2 | 5.5 |
| Total Carbon   | 78.7 | 85.8 | 65.12 | 69.02 |
| Fixed Carbon   | 71.36 | 30.2 | 57.5 | 55 |
| Sulphur        | 0.32 | 2.0 | 0.54 | 0.59 |
| Hydrogen       | 1.0 | 7.13 | 1.14 | 1.4 |
| Surface area (m²/g) | 7.2 | 10.32 | 11.36 |

Table 2. Ash analysis of the carbonaceous materials used in the present study.

|                | Ash analysis by XRF (%) |                |                |
|----------------|------------------------|----------------|----------------|
|                | Components | Metallurgical coke | Waste rubber tyre |
| Silicon as SiO₂ | 50.7 | 27.94 |
| Iron as Fe₂O₃ | 4.8 | 0.14 |
| Aluminium as Al₂O₃ | 36.0 | 3.13 |
| Calcium as CaO | 3.3 | 8.38 |
| Magnesium as MgO | 0.94 | 1.35 |
| Sodium as Na₂O | 0.39 | 1.37 |
| Potassium as K₂O | 0.53 | 0.05 |
| Phosphorous as P₂O₅ | 1.6 | Nd |
| Sulphur as SO₂ | 0.39 | 7.58 |
| Titanium as TiO₂ | 1.4 | Nd |
| Zinc as ZnO | Nd | 40.81 |
by Onesteel Sydney mill is given in Table 3. After reaction in the DTF, the carbonaceous blends were ground to a fine powder (<60 mm) using a Rocklab rotation grinder fed with compressed air and substrates were compacted in a steel die using a hydraulic press under a load of 7 tonnes. The same procedure was employed for the raw metallurgical coke, which due to its low volatile content was not further devolatilized in the DTF. The compacted, cylindrical substrate had a diameter of 20 mm and thickness of 3–4 mm. This was removed from the die and placed on the alumina sample holder of the sessile-drop experimental assembly. The experimental approach and methodology followed in this study has been reported in a previous paper.\textsuperscript{20}

### 2.2. Carbon/Slag Interactions

Using the sessile drop technique, carbon/slag interactions were investigated at 1550°C in an horizontal furnace provided with a high temperature alumina tube.\textsuperscript{20} This technique is being used to determine carbon/slag interactions and associated nature of the slag foam by continuously monitoring the changes in droplet volume (a measure of gas entrapment) as a function of time. A schematic representation of the experimental setup is shown in Fig. 2. The sample assembly consists of a specimen holder of alumina which was kept in the cold zone of the furnace until the desired temperature (1550°C) was attained and then was subsequently inserted into the hot zone. This eliminated any reaction that could occur at lower temperatures and possibly influence the phenomena to be studied at the temperature of interest. Due to sporadic evolution of gases during carbon/slag interactions, the weight of the slag was selected to be small (~0.055 g). Off gases evolved at the reaction temperature (CO and CO\textsubscript{2}) were monitored using a mass spectrometer. A time delay of about 60 s attributed to the time needed for the gas to travel from the hot furnace to the gas analyser as well as the time needed for the substrate and slag to reach the reaction temperature was noted to exist. The gas data was used to determine the total amount of gases which evolved from the reacting assembly as a function of time. Argon gas ensured an inert atmosphere flowing at a rate of 1 L/min, while the purity of the gas consisted in 99.99% Ar with 2 ppm oxygen present.

Although the reaction between FeO present in the slag and carbon is strongly endothermic (requiring additional energy), the effect of this reaction on the temperature distribution in the sample is not a major concern, since the quantity of slag used is very small (~0.055 g) and the horizontal furnace is designed to ensure isothermal conditions in the hot zone throughout the experiment.

The melting of slag marked the beginning of the contact time. A charge-coupled device (CCD) camera fitted with an IRIS lens was used to capture the live in-situ phenomena in the furnace and a digital video recorder (DVD) connected to the television allowed recording the entire experiment as a function of time. Dynamic changes in volume were determined from the captured images with the help of computerized data processing software. As an approximation, the slag droplet on the substrate was assumed to have a truncated spherical shape. Minor deviations from a spherical shape caused by continuous or sudden evolution of gases were neglected (estimated error ~5% volume). To quantify the changes in slag volumes, a circular marquee was fitted manually to provide a best fit to the shape of the slag droplet, and the centre “O” was identified (Fig. 3). By manually clicking on points “p1” and “p2”, the coordinates of the three data points (p1, p2 and O) were recorded automatically. The details of this software are given elsewhere.\textsuperscript{21}

The volume of the slag droplet and the contact area was computed in terms of the radius ‘r’ of the droplet and the truncated height ‘h’ as a function of time (Fig. 3). Since the weight of slag used was very small (~0.055 g), the effect of gravity was negligible and the volume ‘V’ of the segmented sphere is given by Eq. (1):

$$V = \frac{\pi}{3} (4r^3 - h^2(3r - h)) \quad \cdots \cdots \cdots \cdots \cdots (1)$$

While it is difficult to measure the absolute volume of the droplet in the absence of a reference marker, the sessile-drop slag foaming software generates volume ratio “$V/V_0$” as a function of time, where $V_t$ and $V_0$ represent the volume

| EAF slag composition | Weight percentage (%) |
|----------------------|-----------------------|
| CaO                  | 29.6                  |
| FeO\textsubscript{2}  | 34.8                  |
| Al\textsubscript{2}O\textsubscript{3} | 8.4                  |
| SiO\textsubscript{2}  | 13                    |
| MgO                  | 9.4                   |
| MnO                  | 5.7                   |
at time $t$ and the volume of the slag at the initial stage, respectively.

### 2.3. Interfacial Phenomena

Cross sections of the slag droplets which reacted for different time periods of 1, 2, 4, and 8 min with the employed carbonaceous substrates, were studied by optical microscopy. This was possible by closely monitoring the reaction time after the initial melting of the slag. For optical tests the carbon/slag assembly was mounted in an epoxy resin and then dried to remove the possible moisture, followed by polishing. The samples were observed under the optical microscope to investigate the distribution of gas bubbles trapped within the slag droplet and the generation of metal droplets as a result of iron oxide reduction.

### 3. Results

#### 3.1. Off-gas (CO, CO$_2$) Generation

The output from the off gas analyser consists of ppm values of CO and CO$_2$ evolved during the high temperature reaction between the carbonaceous substrate and slag, specifically iron oxide reduction by carbon. The total amount of removed C is calculated as a function of time and presented as cumulative values, assuming that the generated gases consists of only CO and CO$_2$ 

$$
\text{cumulative total gases generated (vol\%)} = (\text{CO } \text{vol\%}) + (\text{CO}_2 \text{ vol\%})
$$

Argon gas (99.99% purity) was continuously purged through the furnace, to ensure an inert atmosphere. Even though it contained <2 ppm oxygen, this is considered to have no significant effect on both the reactions in this system, and on changes in the gas volume as detected by the IR gas analyser. Extensive work conducted by Mehta, Siddiqi under the same experimental conditions on carbonaceous substrates clearly show that the presence of oxygen in Argon could be neglected due to the comparatively very high volumes of off-gases (CO and CO$_2$) produced from the reactions. Figure 4 shows the total removed gases produced from metallurgical coke and its blends with Rubber when in contact with the EAF slag. The variations in amounts of removed carbon, i.e. the amount of evolved oxides, show an increase with increasing the rubber content of the blend. By direct observation of the graph, we may notice that the lowest amount of removed C occurs in the raw coke, increasing in Blend 1, while a further noticeable increase was seen when Blend 2 containing more rubber in its composition was used. Three distinct stages can be identified from the figure: i) an incubation period due to initial time taken for heating of the substrate and the slag after insertion into the furnace hot zone, ii) a steady state reaction region from where the rate constant can estimated, followed by iii) the third stage consisting of a slowing down period due to local deficiency of CO and CO$_2$ gases. Qualitatively, the rate of the slope of the second stage increases when coke is mixed with Blend 1, while a further increase is observed when more Rubber is added to the Blend 2. This indicates that the rate of reduction of iron oxide is enhanced as the proportion of rubber in the blend is increased.

In the reduction of iron oxide, it is assumed that all Fe$_2$O$_3$ is firstly converted to FeO, followed by further reduction of FeO to Fe. The reduction of FeO to Fe takes place at a slower rate. Since the reduction of Fe$_2$O$_3$ to FeO is assumed to occur quite rapidly, it has not been considered in our calculations.

The off-gas measured results from the iron oxide-rich slag reacting with various carbonaceous materials and this is quantified for the reduction reaction. Figures 5(a)–5(c) provides the generated gas concentrations (vol%) in terms of CO and CO$_2$ gases resulting from the interaction of the EAF slag with coke and its corresponding rubber blends.

The gas generated from the above mentioned reaction will form bubbles at the carbon/slag interface leading to the formation of a gas film. The maximum amount of oxygen that can be removed from the slag and the ash present in the carbonaceous substrate is calculated in terms of the number of moles of oxygen. For these calculations, the volumes of CO and CO$_2$ are converted into equivalent number of moles of oxygen removed from the oxides, considering that each mole of CO evolution corresponds to 1 mol of oxygen re-

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**Fig. 5.** Generated gas concentrations (vol%) in terms of CO and CO$_2$ gases resulted from the interaction of the EAF slag with (a) coke, (b) Blend 1 and (c) Blend 2.

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moved from the system, while each mole of $\text{CO}_2$ accounts for 2 mol of oxygen.

The oxygen content in the off-gases produced by the reduction reaction is believed to be accounted for the reduction of FeO in the slag. However, the authors are in progress of submitting a paper focusing on reduction rate kinetics for a much wider range of experimental conditions.

3.2. Carbon/Slag Interactions

All experimental runs were recorded up to 30 min, but due to insignificant changes in the slag volume after 700 s no more data points are presented after 700 s. In order to qualitatively visualize the foaming phenomena, a few representative dynamic wetting images of the slag droplet with metallurgical coke and its blends with lower and higher concentration of rubber are shown in Figs. 6(a)–6(c). The size of the slag droplet in contact with metallurgical coke (Fig. 6(a)) did not show a significant variation with time during the initial stages and moreover, with time, the slag droplet fluctuated to small extents in volume and maintained a reasonably spherical shape. The small fluctuations in droplet size are associated with the generation and subsequent release of gases. The EAF slag reacting with Blend 1 increased in volume and attained a spherical shape. Fluctuations appeared throughout the experiment, showing an improvement in volume when compared to coke alone (Fig. 6(b)), when Blend 2 (Fig. 6(c)) replaced the straight coke usage; the slag attained the spherical shape in a very short period of time and showed an increase to a certain extent after 240 s of reaction. Images were captured for every 5 s during the initial stages of contact and every 30 s during later periods.

In order to quantify the changes in volumes of the samples in this study, $V_t/V_0$ was computed and plotted as a function of time (Fig. 7). The ratio corresponds to the slag volume attained at time $t$ ($V_t$) and the volume ($V_0$), accompanying the initial slag melting stage is represented by $t=0$, the volume ratio starts with a value of 1; following this initial stage, changes are observed corresponding to CO and $\text{CO}_2$ generation and entrapment, which is reflected in an increased droplet volume. After a certain period of time, gas activity has reduced considerably with nearly stable $V_t/V_0$ values.

The graph reveals the volume ratio, $V_t/V_0$, of the slag reacting with metallurgical coke recording an initial value of 1.0; with time it decreased without any sudden changes to 0.5. This indicates a lower extent of gas entrapment by the slag. For Blend 1 the slag volume ratios showed significantly different trends with much higher levels of droplet volumes in the first 400 s of reaction. The volume ratio $V_t/V_0$ showed fluctuations, with the drop growing up to about at a ratio of 2.2 due to the gas trapped within the slag, dropping down to a value of 1 after 600 s with the release of gas and consumption of C. This indicates that the decrease in slag volume took much longer when Rubber was mixed with metallurgical coke, in Blend 1, suggesting significant levels of gas entrapped and subsequently released during carbon/slag interactions. The slag droplet was continuously
changed with the evolution of CO and CO₂ gases. When the rubber proportion in the blend increased as in the case of Blend 2, the volume ratio decreased as compared to Blend 1 but in fact maintained a steady value which was higher than that obtained when coke is the carbon material. For Blend 2, the rate of gas generation increased, as shown in Fig. 4, therefore lower extent of gas was retained in the slag compared to Blend 1.

The EAF steelmaking furnace creates dynamic and non steady state conditions. The continuous formation of gases and associated slag foaming changes significantly as a function of time depending on slag chemistry and operating conditions, thus the fluctuating behaviour needs to be considered. The method and experimental setup used here has been published recently in ISIJ International by Rahman, Sahajwalla et al. and has been successfully applied to compare conventional materials. The publication in Steel Research Int. by Sahajwalla et al. considered besides the normally used coke, different blends with waste plastics and the technique proved to possess a series of advantages. The visual monitoring of carbon–slag interactions for investigation of interfacial phenomena with further data processing of video images through the novel sessile drop software detailed by Khanna et al. in a Met. Trans. communication has significantly extended the capacity of this technique towards rapid and quantitative estimation of gas entrapment in the EAF slag matrix.

3.2.1. Physical Properties of Steelmaking Slag

A review paper by Mills and Keene on the transport phenomena in complex steelmaking slags containing FeO, CaO, MgO, SiO₂, and MnO as the major components, reported that the density of complex slags is highly influenced by the iron oxide content as shown by the correlation given by Eq. (2):

\[ \rho = 2460 + 18 \cdot \text{wt\%FeO (kg/m}^3) \] ...............(2)

Turkdogan modified the equation in the previous study for the case when MnO is present in the system. Considering that the densities of FeO–SiO₂ and MnO–SiO₂ are essentially similar, the equation was developed considering the average of the data represented in terms of (%FeO + %MnO).

\[ \rho = 2460 + 18 \cdot \text{(wt\%FeO + wt\%MnO) (kg/m}^3) \] .......(3)

Where: \( \rho \) represents the slag density in kg/m³.

Additionally, surface tension data of complex slags at steelmaking temperatures were normalized using the respective temperature coefficients and the following expression (Eq. (4)) was derived.

\[
\sigma = 0.75424 - 0.5694 \left( \frac{\%\text{SiO}_2}{100} \right) - 0.13713 \left( \frac{\%\text{FeO}}{100} \right) (N/m) \quad \text{.........(4)}
\]

Where: \( \sigma \) is the surface tension (N/m).

It is evident that an assumption is involved in this derivation, such that complex slag chemistry is simplified to a pseudo-binary CaO–"FeO–SiO₂" system and a constant temperature. A similar assumption has been considered by Morales et al., for a comparable slag system consisting of (SiO₂ + Al₂O₃)–(CaO + MnO + MgO)–FeO proving that the presence of minor components, such as Al₂O₃, MnO and MgO would not significantly change the surface tension values.

The evaluation of the surface tension and density according to this model is possible through calculations of partial molar volumes of FeO, SiO₂, and MnO, respectively, which are interdependent on the values of FeO consumed by the reduction reaction. Assuming, the reduction reaction occurs for only FeO, the amount of silica and MnO in the slag will increase proportionally with decreasing FeO concentration. Although the reduction of FeO in the slag takes place in a short period of time it does not influence the changes in surface tension significantly. The surface tension values only change from 0.628 to 0.633 N/m, with the highest increase being attributed to Blend 2 (Fig. 8(b)).

The slag density was calculated using Eq. (3) and appears to be in accordance with the computed surface tensions, implying that the values do not vary in a wide range, decreasing from 3.1 g/cm³ to the lowest density of 2.5 g/cm³ developed by the same Blend 2 after the reduction reaction was completed (Fig. 8(a)).

3.3. Interfacial Phenomena

Figures 9(a)–9(c) show optical microscopy images of the cross-sections of quenched carbon/slag assemblies exposed to 1550°C for times ranging between 1–8 min. In Fig. 9(a) polished metallurgical coke/slag assembly is presented after 1, 2, 4 and 8 min of reaction. It can be noticed that even from the 1st minute of contact, fine iron particles are being formed and dispersed throughout the slag. Moreover, at the
carbon/slag interface circular regions of iron with diameters close to 250–400 μm are seen. Few small gas bubbles trapped within the slag droplet are seen along with one large bubble observed in the first minute of reaction. After 4 min of contact, the interfacial region between slag and coke shows reduced iron containing region with a diameter 500 μm.

A close inspection of the cross section of slag/Blend 1 sample revealed significantly different behavior (Fig. 9(b)). From the figure, large numbers of gas bubbles of small diameter are dispersed throughout the entire slag volume. The metallic iron appears mostly at the slag/gas interface and the overall slag volume is dictated by large number of small bubbles. With elapsing time, the small gas bubbles still appear, although not as numerous as those observed during the initial stages of reaction. The evolution of gases is obvious and occurs due to the reaction of carbon with the FeO in the slag droplet, resulting in release of CO and CO2 gases. These gases participate in volume fluctuations of the slag droplet, while Fe is deposited at the slag/gas and slag/carbon interface. At the latter stage of reaction the reduction was complete with the molten metal resting at the interface appearing as bright round droplet. An initial big gas bubble along with small diameter bubbles are entrapped in the slag volume when blend 2 reacted with the EAF slag (Fig. 9(c)). With increasing reaction time gases are still present in the slag droplet. With the reduction of iron oxide in slag nearing completion, the molten iron droplets tended to increase in size and precipitated on the substrate.

Gas entrapment in metallurgical slags as a result of carbon–slag interactions is a random and probabilistic phenomenon due to its dynamic nature. A continuous/sporadic evolution of gases in the droplet shape and size makes it very difficult to yield valuable/reliable information. However, the recording videos and snap shots monitored using the present technique offers information to support the gas behaviour, mainly its entrapment and release. A qualitative slag droplet profile, through detailed optical analysis might explain the gas behaviour, meanwhile the formation of metal becomes obvious and the foaming and reduction phenomena are explained in a continuous matter.

4. Discussion

The chemical reaction that is primarily responsible for carbon/slag interactions is:

\[
\text{FeO}_{\text{slag}} + C_{(s)} = \text{Fe}_{(metal)} + \text{CO}_{(g)}
\]

As the reaction of the slag components (mainly FeO) with C starts, CO bubbles were found at the slag/metal interface. Previous studies have shown that a gas ferrying mechanism describes the reaction between solid carbon and iron oxide due to the fact that the 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 gets ferried back to carbon, where gasification of CO2 to CO takes place via Boudouard reaction as follows:

\[
\text{CO}_2 + C = \text{2CO}
\]

Due to the coexistence of the dispersed gas layer and foam layer, the entire slag bath becomes foamy. Bubbles of different dimensions are formed which start to evolve depending on their sizes and the physicochemical properties of the reacting slag. The rate of CO and CO2 gases generation depends to a great extent on the carbon based material and their composition, i.e., volatile matter and ash content in addition to slag properties and process conditions such as temperature. While the total amount of removed gases for raw Metallurgical Coke was obviously lower than that obtained when Blend 1 was used as carbonaceous substrate, by enhancing the rubber content in the blend a further increase was obtained when Blend 2 was used. The higher amount of (CO2) generated by the polymeric blends could be attributed to a certain extent to the volatiles still trapped in the carbonaceous mixtures, which are available after the initial combustion reaction in the DTF. These unburned volatiles could be represented by CH4 gas that at the temperature of the tests (1 550°C) transforms into CO and H2/CO2 and H2O.

As the decomposition reaction of CH4 shows, 1 mol of carbon corresponds to 2 mol of hydrogen, thus with every mole of carbon, 2 mol of H2 are getting released. Reduction with H2 has been considered by different researchers to be much faster than reduction with CO and CO2 gases, of the order of one or two magnitudes faster, thus the rubbers...
kinetic advantage might come from its richer hydrogen content, in comparison to metallurgical coke, because the reduction reaction \((\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O})\) is much faster than \(\text{CO}\) reduction. Hydrogen content in the rubber has been measured in Amdel laboratories and Table 1 provides the values.

The rate of gas generation is enhanced when coke/rubber blends are compared to coke alone (see Fig. 4). Higher gas generation for Blend 2 leads to higher flow rate of gas, increased velocities with less gas being entrapped in slag compared to Blend 1.

Another factor that could influence the total amount of generated gases could be the ash content available on the surface of the carbon based substrate. With ash present in metallurgical coke as well as in the combusted rubber blends a 2-D interconnected network along the surface can form. The \(\text{CO}\) 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 ready for further reactions and further bubble formation. When rubber is added, \(\text{CO}\) and \(\text{CO}_2\) bubbles are generated to a higher extent with increasing polymeric amount in the blend.

With \(\text{FeO}\) decreasing the amount of \(\text{SiO}_2\), \(\text{MnO}\) and the other oxide components increase in the slag. The physicochemical properties such as viscosity, density and surface tension are subject to changes. Mills and Keene model was employed for the estimation of surface tension and slag density for \(\text{CaO–FeO–SiO}_2\) system. There is a slight increase of surface tension due to change in slag composition as shown in Fig. 8(b). This will influence to a small extent the size of the bubbles formed during the dynamic interactions. Sulphur could also have an important role to play in suppressing slag foaming as its presence tends to increase the size of \(\text{CO}\) bubbles, affecting the slag stability. Concerning the addition of sulphur, Kozakevitch and Gaskel and Skupien concluded that surface tension will increase. However, with the use of rubber containing blends the volume ratio of slag is seen to be enhanced compared to coke alone, even though higher level of sulphur is present in the blends. The enhanced slag volume and the improved stability of the slag when rubber containing blends are used could be attributed to the higher levels of volatile matter. The analysis presented in Table 1 clearly show that rubber containing blends have higher volatiles which are primarily hydrocarbons and these can contribute towards sustaining higher slag volumes. They can also enhance the reduction of iron oxide which is confirmed in this study through the off gas measurements in Fig. 4. However, as the proportion of rubber in the blend increases, higher level of sulphur in the slag are to be expected, which will ultimately influence the stability of the slag foam as a result of larger \(\text{CO}\) bubbles which will tend to escape faster. Consequently, Fig. 7 shows that the slag volume ratio has decreased for Blend 2. Therefore, the addition of rubber into the coke-rubber blend needs to be optimized depending on the composition of the carbonaceous materials, specifically factors such as volatile matter, ash and sulphur content. In addition, slag composition and its influence on slag properties will also influence carbon/slag interactions.

Balance between reduction and gas entrapment must be established for improving the furnace efficiency and decreasing the energy losses. An increased \(\text{FeO}\) content decreases viscosity and slag density and therefore the ability of the slag to foam is hindered. On the other hand, higher \(\text{FeO}\) content generates an increased amount of gases from reduction and decarburization reactions, leading to enhanced chemical reactions. Large volumes of \(\text{CO}\) and \(\text{CO}_2\) gases are produced and the slag shows an improved gas entrapment. Thus, good physical properties of slag are necessary conditions for foaming but not sufficient alone for establishing a desirable foam. Another condition which should be fulfilled is the sufficient generation of a large amount of gas.

Our results indicate that both, carbonaceous materials properties and their optimum interaction with slag control interfacial reactions between carbon and slag, which are essential for maintaining foaming through generation and subsequent retention of trapped gas bubbles within the slag.

5. Conclusions

This study has shown that blends of rubber with metallurgical coke could be used to partially replace some of the conventional metallurgical coke used in EAF steelmaking for its carbon requirements as a result of enhanced carbon/slag interactions obtained when rubber containing blends are used. Key results are summarised below:

(1) Significant carbon/slag interactions occurred when coke/rubber blends were used, with associated iron oxide reductions within the slag phase. The gases evolving from metallurgical coke showed lower concentrations in comparison to those from the coke–rubber blends. This could be attributed to a certain extent to the volatiles still trapped in the carbonaceous mixtures, which are available after the combustion reaction in the DTF. Also greater generation of gases could arise from the higher rates of \(\text{FeO}\) reduction when coke–rubber blends were used compared to coke alone.

(2) Higher gas entrapment in the slag was also observed when the rubber partially replaced the coke. The size of the slag droplet showed wide fluctuations with time and was associated with trapping and subsequent release of gases.

(3) The present study has brought out the significant role played by both carbonaceous materials and the influence of their fundamental characteristics on various aspects of carbon/slag interactions, including \(\text{FeO}\) reduction, gas generation and its entrapment within the slag as well as the associated enhancement of the slag volumes.

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