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Recycling End-of-Life Polymers in an Electric Arc Furnace Steelmaking Process: Fundamentals of Polymer Reactions with Slag and Metal

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ABSTRACT: Research on the use of waste polymeric materials is one of the solutions for developing environmentally friendly recycling processes for steelmaking. Different polymeric materials [i.e., rubber, high-density polyethylene (HDPE), polyethylene terephthalate (PET), and Bakelite], which have different chemical structures and compositions, were selected for this study as carbon resources. The rapid heating to high temperatures provided during steelmaking will break down the polymeric chains and reactions with liquid slag, enabling gas formation. The dynamic changes in the volume of the slag droplet while in contact with the coke/polymer substrates are measured. Significant levels of gas generation and entrapment are present, leading to an improved performance over coke. Carbon/metal reactions were studied by measuring carbon and sulfur pick-up by liquid metal as well as the formation of reaction products at the metal/carbon interface. The measured carbon pick-up value after 2 min of reaction for metallurgical coke was approximately 0.08 wt %, whereas 100% polymers, such as PET and HDPE, showed an increased value of >2 wt %. The proportion of sulfur pick-up was very similar. The formation of interfacial products, in the case of Bakelite–coke blends, was studied, and the presence of CaCO₃ used as a filler was seen to influence the chemical properties of the carbonaceous substrate. This study has established fundamentals of the interaction of waste polymers with slag and metal in the steelmaking process.

1. INTRODUCTION

Plastics and rubber are accumulating at a rate that reflects the strength of the economy and the intensity of trade and transportation. Billions of waste polymeric materials are discarded around the world; much of the waste is still deposited in landfill sites, while the most common solution relies on incineration. In both cases, because of their resistance to biodegradation and formation of pollutant polycyclic aromatic hydrocarbons upon incineration, plastics and rubbers are a risk to human health and earth.

The use of waste plastics and rubbers in iron- and steelmaking industries has received increased attention based on the high amount of carbon and hydrogen present in polymeric materials. In Japan, Nippon Kokan Co., Ltd. (NKK) developed a process where shredded polymer wastes are mixed directly with the blast furnace burden.¹ Waste tires are treated in electric arc furnace (EAF) plants operated by Nippon Steel Corporation (NSC) Hirohata Ironworks as a substitute for part of the coal and iron scraps.² The steel cords present in the waste tires are melted and recycled into steel, while the carbon in rubber is used as a component of melt pig iron. Asanuma et al.³ used plastic–coal blends in blast furnaces. In Europe, Stahlwerke Bremen substituted coke, at an industrial scale, coal, and heavy oils with end-of-life plastics.⁴ End-of-life tires were charged in the molten steel bath from the top of the furnace tires at the Laminés Marchands Européens (LME) site in Trith-Saint-Leger, France.⁵

More recently, Sahajwalla et al.^{6–9} conducted research on the use of high-density polyethylene (HDPE) plastics and rubber tires as partial replacement of coke in EAF steelmaking using the sessile-drop method. Successful industrial practices followed the

laboratory investigations, leading to improved performance of the EAF practice through better slag foaming, lower power-on time, and decreased energy consumption when plastics and rubber replaced the straight coke usage.

In EAF steelmaking, a foamy slag prevents excessive heat transfer to the furnace roof and sidewalls, making the furnace more efficient and preventing damage to the water-cooled panels from the arc flare. The slag intercepts the energy radiated from the arcs, typically half the energy generated, and the heat is subsequently transferred to the steel. The phenomenon is influenced by two main factors: (1) rate of gas evolution by the reduction reactions and (2) retaining the gas bubbles within the slag layer.

The rates of material devolatilization are important because a faster removal of volatiles might affect the structure of the residual particle and, thus, the subsequent reactions with the slag.^{6,8,10,11} A faster rate of devolatilization will release volatiles much earlier; as a result, less volatiles are available to sustain subsequent reaction in the slag phase. A slower rate allows for a steady release of volatiles, promoting gasification of the carbonaceous blends, allowing for a more effective use of gases in the forthcoming slag/carbon reactions. In addition, when the carbonaceous blends are heated rapidly, the evolution of volatiles may cause pore formation, a surface area increase, and consequently, a

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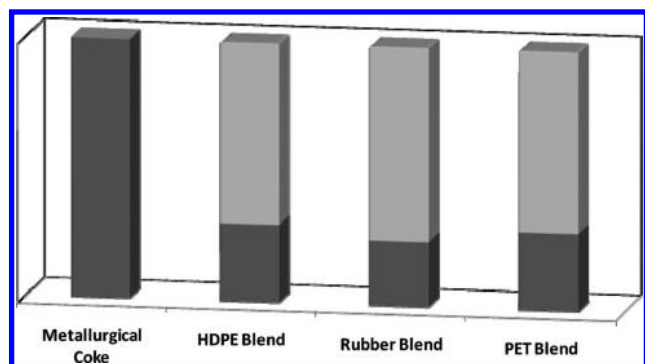


Figure 1. Carbonaceous material composition used for carbon/slag reactions.

higher rate of the $(\text{FeO})-\text{C}$ reaction, resulting in more gases and better slag foaming. A significant reaction in iron- and steelmaking is the dissolution of carbon into molten iron. Several studies have focused on the dissolution of carbon from both graphitic and non-graphitic materials into Fe and Fe–C alloys.^{12–24}

The sessile-drop technique has been used in the past to study the dissolution of carbon from graphitic and non-graphitic materials into pure iron at 1550 °C.^{25–28} Interface studies revealed that ash oxides may act as a physical barrier layer, hindering the dissolution of carbon into the molten iron.²⁶ Cham et al.²⁵ studied the carbon dissolution from different types of metallurgical cokes (MCs) at 1550 °C using the carburizer cover method and reported that the carbon content in the liquid iron ranged from approximately 2 to over 5 wt %. These authors concluded that the ash composition was a dominant factor that influenced the rate of carbon dissolution from cokes. The aim of this study is to develop a fundamental understanding of carbon/slag and carbon/metal interactions in EAF steelmaking while replacing the conventional materials with polymers. Off-gas evolution and variations of volume ratios of the foamy slag with time were measured under reaction conditions, to develop an understanding of the role of gas-entrapment phenomena on the interfacial behavior. Meanwhile, metal–carbon reactions were investigated by determining the dissolution of carbon into liquid iron. The formations of reaction products at the metal/carbon interface are discussed in detail to establish their association with carbon dissolution phenomena.

2. EXPERIMENTAL SECTION

2.1. Sample Selection and Preparation. Polymeric materials, such as HDPE, polyethylene terephthalate (PET), Bakelite, and recycled tires, were selected for studies with slag and metal reactions. MC was chosen as the base material because it is the typical carbon injectant used at OneSteel EAF, Sydney Steel Mill, Australia. HDPE and Bakelite arrived as pellets and were crushed in a specially designed plastic crusher (model Pulverisette 15, Fritsch GmbH, Idar-Oberstein, Germany) and sieved to particle sizes similar to those of coke. PET was taken from a series of plastic bottles, and recycled rubber was cryogenically ground to the desired particle size. 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.

2.2. Polymer Slag Reactions. The polymeric materials designed for the slag reaction were premixed to ensure a compact homogeneous blend. The mass of the carbonaceous substrate was constant for all of the

blends, i.e., 1.6 g. The carbonaceous blend compositional chart is presented in Figure 1.

The elemental analyses of the basic components present in the carbonaceous blends are summarized in Table 1. For slag-foaming experiments, an EAF slag was provided by OneSteel, Sydney, Australia. The chemical composition of EAF slag is shown in Table 2.

The experimental procedure involved three parts: (i) reactions in a custom-made horizontal furnace at 1550 °C, (ii) visual observation using a charge-coupled device (CCD) camera, and (iii) off-gas analysis using a gas chromatographic (GC) analyzer [SRI 8610C chromatograph multiple gas 3 GC configuration equipped with a thermal conductivity detector (TCD)] and a continuous infrared gas analyzer. Approximately 1.6 g of the powder was put in a die and then compacted under a load of 7.5 kN with the aid of a hydraulic press, resulting in a carbonaceous substrate with a top surface area of 3.14 cm². The EAF-rich slag was placed on the top of the substrate and further placed on an alumina/graphite holder of the sessile-drop experimental assembly.

2.3. Polymer Metal Reactions. For the carbon metal reaction, Bakelite–coke blend and three plastics were used (HDPE, PET, and Bakelite). The chemical composition of the 100% materials is presented in Table 1. Blends of HDPE and PET as well as 100% plastics were used in polymer–metal reactions, and a comparison to pure coke is also provided. Because ash is quite important in the carbon–metal reaction, a detailed analysis on the ash composition of the materials is presented in Table 3. An amount of 0.5 g of electrolytic pure iron (99.98% Fe) commercialized from Sigma Aldrich was placed on the coke–plastics/100% plastic samples. Carbon dissolution experiments were carried out using the sessile-drop technique in a horizontal tube furnace.

2.4. Sessile-Drop Arrangement for Carbon/Slag and Carbon/Metal Studies. Slag-foaming and carbon dissolution experiments were carried out using the sessile-drop technique at 1550 °C in a horizontal tube furnace. This technique has been previously used to study slag/carbon interactions, including slag foaming, carbon liquid iron reactions, as well as the wettability and iron oxide reduction with graphite, coals, chars, and cokes.^{6–8,19,23,25}

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. Because of 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 CO₂) were monitored using a mass spectrometer/GC analyzer. The gas data were used to determine the total amount of gases, which evolved from the reacting materials 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 of 99.99% argon with 2 ppm oxygen present.

Although the reaction between FeO present in the slag and carbon is strongly endothermic, the effect of this reaction on the temperature distribution in the sample does not pose a major concern, because 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. Dynamic changes in the volume were determined from the captured images with the help of computerized data processing software.²⁹

The carbonaceous blends were ground in a ring mill to obtain a fine powder, which was sieved to a particle size <40 μm, whereas 100% plastic materials were ground using a plastic crusher to a similar particle size. Approximately 1.6 g of the carbon powder was put in a die and then compacted under a load of 7.5 kN using a hydraulic press. The technique used in the present study was not to maximize the dissolution of carbon into metal but to obtain an indication of dissolution from polymeric

Table 1. Elemental Analysis of MC, HDPE, Rubber, and Bakelite

components	100% MC ^a	100% HDPE	100% rubber	100% PET	100% Bakelite
carbon (%)	77.7	85.5	85.48	62.5	53.4
hydrogen (%)	1.11	14.2	6.96	4.2	4.0
sulfur (%)	0.28	0.3	1.68		0.02
nitrogen (%)	1.21		0.25		
oxygen			6.7	33.3	11.6
calorific value (MJ/kg)	28–31	46.5	40.16	23.6	

^a Analysis performed by Amdel Laboratory and Technical Services, New South Wales, Australia.

Table 2. Chemical Analysis of the EAF Slag Used in the Present Study

oxide type	CaO	Fe ₂ O ₃	Al ₂ O ₃	MgO	SiO ₂	MnO
(wt %)	31.1	33.9	6.1	10.7	13.0	6.2

Table 3. Chemical Analysis of the Ash Composition for Coke and Polymer Blends Considered in the Present Study^a

ash composition (wt %)	MC	HDPE blend	rubber blend	PET blend	Bakelite blend
SiO ₂	61.10	60.90		59.80	47.30
Al ₂ O ₃	32.10	31.40		31.40	22.80
Fe ₂ O ₃	1.60	2.10		2.10	2.20
CaO	0.71	0.86		1.40	18.30
P ₂ O ₅	0.68	0.72		0.70	0.52
TiO ₂	1.00	1.10		1.00	0.77
MgO	0.17	0.24		0.34	1.70
K ₂ O	0.29	0.30		0.33	0.35
Na ₂ O	0.19	0.22		0.53	0.18
SO ₃	0.13				
CaCO ₃					

^a Analysis performed by Amdel Laboratory and Technical Services, New South Wales, Australia.

materials. Carbon and sulfur picked up by the metal droplets were measured using a carbon–sulfur analyzer (LECO 230, C and S analyzer).

Because the primary focus of this work was on a quantitative estimation of rapidly changing droplet volumes and slag foaming, the slag droplet on the substrate was assumed to have a truncated spherical shape. The data from all images were stored in a data file for further processing.

2.5. Interfacial Phenomena as a Result of Carbon/Slag Reactions. 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, dried to remove the possible moisture, and polished using a wide range of SiC-graded papers. 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.

2.6. Interfacial Phenomena as a Result of Carbon/Metal Reactions. The reaction products situated at the carbon/metal interface after 4 and 60 min of contact were investigated using a scanning electron microscope (SEM) Hitachi (S3400-X) coupled with energy-dispersive X-ray spectroscopy (EDS).

3. RESULTS AND DISCUSSION

3.1. Characteristics of Polymeric Materials and Coke. The polymeric materials used in the blends vary in chemical structure and composition, including thermosets, thermoplastics, and elastomers composed of either simple carbon, hydrogen backbones, or more complex structures incorporating oxygen.

The X-ray diffraction (XRD) patterns of the materials are reported (Figure 2), and a significant difference in the structure of the materials was seen, such that coke had an intermediate structure between graphitic and amorphous with a high silica peak, suggesting the presence of high ash content. HDPE is a predominant crystalline material with sharp characteristic peaks, whereas PET is semi-crystalline polyester with a very distinctive peak. Rubber is well-known for its broad diffused spectrum with asymmetric features, and its structure is associated with packing of aliphatic side chains or condensed saturated rings.

3.2. Fundamentals of Coke/Polymer Reactions with Slag. The EAF steelmaking furnace creates dynamic conditions. The continuous formation of gases and associated slag foaming changes significantly as a function of time depending upon slag chemistry and operating conditions.

The gas-entrapment phenomenon has been quantified using the sessile-drop arrangement, and the novel processing software detailed above was used for estimation of slag volume ratios as a function of time. This technique has been accepted and extensively used.^{6–9} To qualitatively demonstrate the slag-foaming behavior, a few representative dynamic images of the slag droplet in contact with MC and its blends with rubber and HDPE are shown in Figure 3. The size of the slag droplet in contact with MC 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 EAF slag reacting with the HDPE blend showed significantly higher levels of gas entrapment. When the rubber blend replaced the straight coke usage, the slag showed an increase to a certain extent; however, the volume of the slag was similar throughout the experiment. Images were captured for every 5 s during the initial stages of contact and every 30 s during later periods.

To quantify the changes in slag volumes, attributed to formation, entrapment, and release of gases, V_t/V_0 was calculated and plotted as a function of time.

Volume measurements of the coke/rubber mixture (Figure 4b) showed an improvement in the slag foaming in comparison to coke alone, fluctuating around the value of 1 and staying in that vicinity for the remainder of the experiment, suggesting significant levels of gas entrapment and subsequently released during carbon/slag interactions. Results of the HDPE slag-foaming behavior (Figure 4a) showed an improvement in the slag-foaming performance compared to MC and the recycled rubber, fluctuating at high levels. The PET/coke blend (Figure 4c) showed a stable slag-foaming behavior, with the volume ratio fluctuating between 1.1 and 1.3 (average of 1.2) throughout the experiment.

3.2.1. Off-Gas Generation. Off-gas measurements using the infrared analyzer enabled the determination of the amounts of

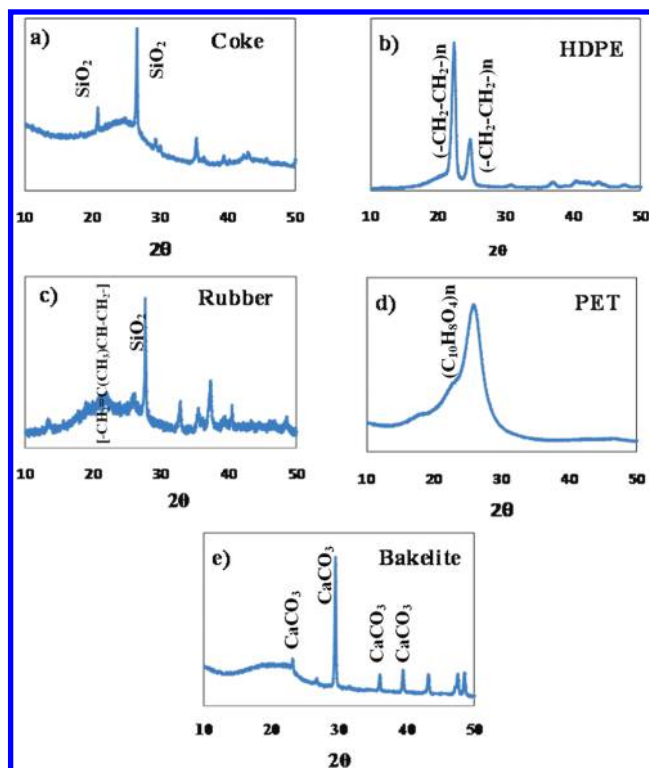


Figure 2. XRD patterns displaying peak intensities of 100% (a) coke, (b) HDPE, (c) end-of-life rubber, and (d) PET plastics.

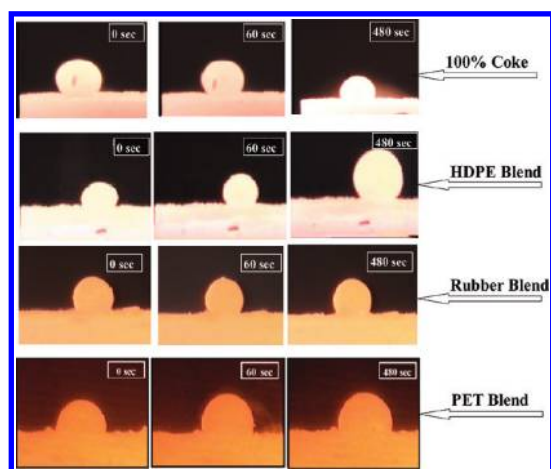


Figure 3. Snapshots of slag droplets in contact with 100% MC, HDPE blend, rubber blend, and PET blend at 1550 °C as a function of time.

CO and CO₂ formed during carbon–slag interactions.³⁰ The rate of gas generation following the interaction of the HDPE–coke blend was seen to be the fastest, followed by the rate of gas generation from rubber–coke blends, while the lowest rate was seen when coke represented the carbon material.⁹ A similar result was found by Dankwah et al.³¹ while using a different approach involving the preparation of an iron oxide/carbon composite pellet. The high amount of CO and CO₂ generated when HDPE and rubber replaced part of the coke could be attributed to a certain extent to the volatiles still trapped in the carbonaceous mixture, which are available after the initial combustion reaction in the drop-tube furnace (DTF). These volatiles are predominantly

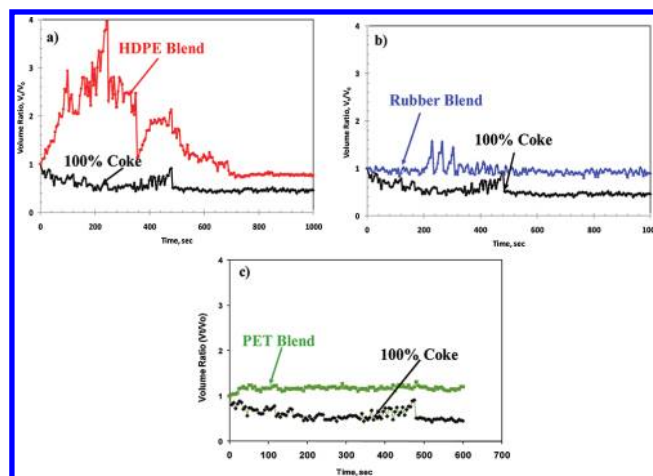


Figure 4. Volume ratio of (a) 100% coke and HDPE blend, (b) 100% coke and rubber blend, (c) 100% coke and PET blend, and 100% coke resting on EAF-rich oxide slag with respect to the reaction time.

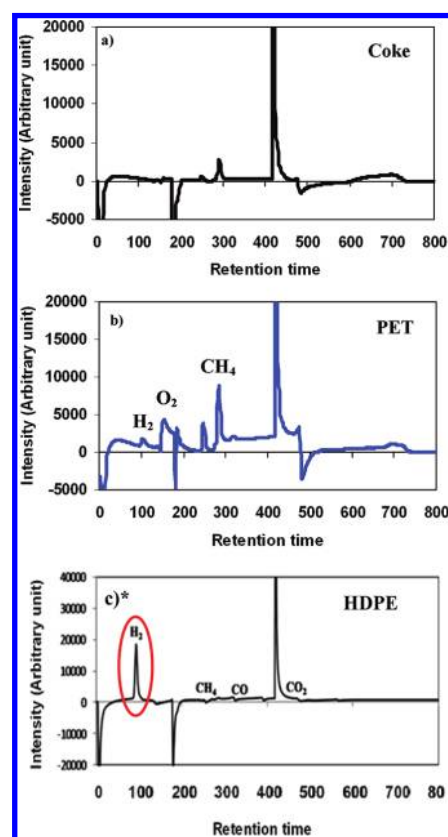


Figure 5. Gas chromatographs showing the gases produced from the different blank substrates of (a) coke, (b) PET/coke blend, and (c) HDPE/coke blend³¹ after 1 min at 1550 °C.

CH₄ gas, which, at the temperature of the tests, transforms into CO and H₂.

When PET was used as the plastic source, the rate of gas generation was very similar to the rate seen when coke was used as the carbon source.³² The estimated rate was based on CO and CO₂ gas generation. The lower level in the case of PET compared to the other polymers could be attributed to the lower concentration of carbon present in PET.

The polymeric materials, including HDPE, rubber, and PET, are expected to have higher volatile matter (VM) compared to coke. Therefore, a further determination of the gaseous species devolatilized from polymer/coke blends during slag/carbon reactions was carried out using a GC analyzer.

The chromatograms of the gases evolved are shown in Figure 5. The HDPE polymer and its corresponding blend showed a high content of H_2 in the off-gas, as seen from the dominant peak.³¹ On the other hand, the chromatogram of coke exhibits a significantly lower content of hydrogen, and this is in good accordance with the previously reported trends.^{31,32}

In the case of the PET/coke blend, O_2 was detected along with H_2 , CH_4 , CO , and CO_2 . PET contains approximately 33.3% oxygen. These results clearly indicate that the differences in the gases generated from plastic/coke blends arise from the differences in the chemical compositions of the polymer. Moreover, they suggest that not only does solid C react with slag but the volatiles from the polymers in the form of CH_4 and H_2 can also participate in the slag reaction, leading to faster reduction of FeO by H_2 .^{33,34} Previous work demonstrated that hydrogen increases the reduction rate by a factor of 2–3 times compared to the reduction rates developed by $CO-CO_2$.³⁴

The plastic/rubber kinetic advantage might come from its richer hydrogen content, in comparison to MC, because the reduction reaction [$FeO + H_{2(g)} = Fe + H_2O_{(g)}$] is much faster than CO reduction.

The rate of gas generation is enhanced when coke/polymeric blends are compared to coke alone.⁹ However, when the proportion of polymeric material exceeds a certain value, as seen in our previous publication,⁹ the flow rate of gases evolved from the coke/polymer blend escapes at a fast rate, increasing its velocities and, thus, allowing a fast passage through the slag. Less gas remains entrapped in the slag, and a poor foaming behavior is seen compared to coke. The generation of gases as a result of slag carbon interactions has been reported to have a significant effect on gas entrapment in the slag phase (slag foaming), and this influence was found to depend upon the basic characteristics of carbonaceous materials, such as chemical composition (i.e., volatiles, ash, carbon content, etc.).

3.2.2. Interfacial Phenomena between Coke/Polymeric Material Blends and EAF Slag. The sample was pushed in the hot zone of the furnace, and the counter started after the slag droplet showed the first sign of melting. After fixed periods of time, the slag assembly was withdrawn into the cold zone of the furnace and samples were quenched to qualitatively visualize the gas-entrapment phenomena. The optical images showed several phases, such as dark regions corresponding to the entrapped gas bubbles, shiny spots representing the reduced iron, and gray regions portraying the slag phase. A close inspection of the cross-sections showed a high amount of iron particles in the EAF slag after the interaction with MC, along with a large bubble observed after the first minute of the reaction.^{6,8} Large gas bubbles were seen when HDPE replaced part of the coke, thus, a fluctuating slag volume. Small gas bubbles characterized the slag droplet when rubber was part of the carbonaceous substrate, hence, a stable slag. A similar behavior was seen when PET was blended with coke and used as the carbonaceous substrate.

In the present study, the polymeric blends contributed to a larger number of gas bubbles entrapped into the slag phase. The size distribution of the gas bubbles plays a very important role on their retention time into the slag matrix. Smaller gas bubbles could promote a better retention, leading to larger slag volumes.³³ An

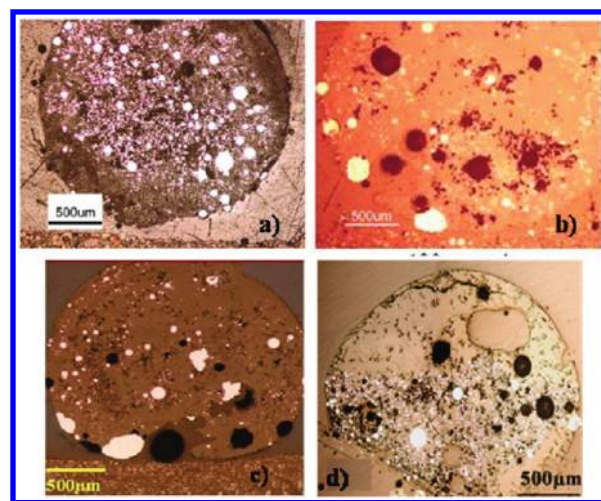


Figure 6. Optical microscopy results on quenched (a) coke/slag, (b) HDPE blend/slag, (c) rubber blend/slag, and (d) PET/slag at 1550 °C.

increase in the bubble size might result in an increase in the gas escape rate.³⁶

Measured bubble diameters from the optical images at different times (Figure 6) are reported in Table 4. The EAF slag following the interaction with polymer–coke blends showed generally smaller bubble diameters compared to coke. PET and the rubber–coke blend had a similar bubble diameter (62 and 63 μm , respectively), and this is consistent with the measured volume ratio, allowing for a stable slag foam for the duration on the experiment. The HDPE–coke blend formed small gas bubbles in the slag matrix, promoting a large fluctuation of the slag volume, as seen in the estimated volume ratios (Figure 6).

3.3. Fundamentals of Coke/Polymer Reactions with Metal.

The variation in carbon and sulfur picked up by liquid steel as a function of time for coke, coke/Bakelite blend, and 100% plastics is measured in the present study to determine the influence of ash and VM present in these carbon-based materials on carbon dissolution (Figure 7).

3.3.1. Influence of Ash Present in Coke and Bakelite Polymer on Carbon Dissolution. MC allowed carbon pick-up at a slow rate and reached a maximum of 0.1 wt % after 30 min of contact. Little carbon transfer was observed in later stages. Sulfur can transfer to the melt concurrently with the dissolution of carbon. Sulfur transfer from the coke into liquid steel stabilized to 0.05 wt % within a few minutes.

The results are in good agreement with previous studies carried out using the same technique.²³ A study performed by Cham et al.³⁷ showed dissolution values of two MCs into Fe–C melt at 1550 °C to be 1.1×10^{-3} and $14.7 \times 10^{-3} s^{-1}$. The large difference in carbon pick-up values was attributed to the differences in mineral composition and profile of the two cokes investigated. In the present study, the coke used is a poor carburizing material; high ash oxide content in the coke is expected to significantly affect carburization,¹⁴ especially the presence of Al_2O_3 , which accounts for 32 wt % of the ash in the coke sample.

Coke was partially replaced with a defined proportion of the above studied Bakelite plastic (see the bar chart of Figure 1). The Bakelite–coke blend transferred a maximum of ~ 0.19 wt % carbon in metal, a value slightly improved when compared to coke. The blend contains 28.3 wt % ash, with a high proportion of CaO, while the present coke has 17.2 wt % ash, with a significant

amount of Al_2O_3 . The interfacial phenomenon is governed by the presence of ash, and the slight improvement in carbon pick-up when Bakelite replaced part of coke may be due to the difference in ash chemistry. The overall sulfur pick-up was significantly lower than the parent coke, stabilizing at ~ 0.06 wt % after 60 min of reaction. The decreased sulfur pick-up in case of the blend could be attributed to greater desulfurization of the melt, which could have occurred because of the higher concentration of CaO in Bakelite.

The effect of ash on carbon dissolution was also studied while using 100% Bakelite plastic because the presence of ash is significant. Bakelite samples were ground into powder and compacted to make a substrate. The carbon pick-up from raw Bakelite was determined after 1 and 60 min of reaction. A value of 0.082 wt % after 1 min of reaction was measured, which is comparable to that observed from coke alone. The carbon pick-up for the Bakelite was observed to slightly increased thereafter, with the measured carbon content in the metal droplet reaching 0.186 wt % after 60 min. Small sulfur pick-up values by molten steel were observed, and they were attributed to the relatively low sulfur content in the Bakelite used.

The content and composition of the ash in the carbonaceous materials are known to have a strong influence on the dissolution of carbon.^{14,19,25,38} The Bakelite ash content and chemistry are significantly different from those of MC, i.e., 31.0 and 17.2 wt % for Bakelite and coke, respectively. The main component present in Bakelite ash is CaCO_3 , which converts to CaO in the initial stage of the reaction. Besides, relatively low levels of fixed carbon are present in Bakelite and its blend compared to coke (see Table 3). Thus, the differences in their carbon dissolution behavior could be attributed to the differences in the ash chemistry, which played an important role in interfacial reactions. However, because only slight improvements were observed, other polymeric materials, different in chemical composition and structure, are investigated to determine the influence of volatiles on carbon dissolution into liquid metal.

Table 4. Measured Bubble Diameters for Different Samples

sample	minimum bubble diameter, μm ($<100 \mu\text{m}$)		maximum bubble diameter, μm ($>100 \mu\text{m}$)
time of reaction	2 min	8 min	2 min
MC—EAF slag	90.0	93.0	139–308
HDPE blend—EAF slag	29.0	39.0	240.0
rubber blend—EAF slag	63.3	37.5	265.0
PET blend—EAF slag	62.0	36.0	

3.3.2. Interfacial Phenomena between Coke/Polymeric Materials and Liquid Metal. The chemical composition of the materials selected in the present study varies to a high degree (see Table 3), and this is expected to influence the relative proportions of the ash oxide layer formed at the metal/carbon interface. The surface of the metal that was in close contact with the carbon material was investigated by means of SEM imaging coupled with EDS analysis. When coke represented the carbon source (Figure 8), it was found that the interface was predominantly covered by Al_2O_3 , even after 4 min of contact, and this was expected on the basis of the high alumina content present in coke ash (32 wt %). The EDS spectra showed a very small peak of silica, even though silica is the major component of the coke ash. The reduction of silica is one factor that can decrease the level of solute carbon in the liquid metal by converting silica into silicon in the melt.^{17,23} After 30 min of reaction, the ash layer was seen to grow, with the interface showing a high content of Al_2O_3 .

SEM images of the metal/carbon interface along with EDS analysis in the case of the Bakelite blend for 4 and 30 min are shown in Figure 9. Because Bakelite has a high CaCO_3 content, when blending with coke, differences in the ash chemistry are expected. The reaction products formed at the metal/carbon interface in the case of the Bakelite-containing blend appeared to be glassy because of the presence of liquid phases, which were determined to be a combination of CaS and $\text{CaO} \cdot \text{Al}_2\text{O}_3$. The appearance of calcium aluminates ($\text{CaO} \cdot \text{Al}_2\text{O}_3$) at the interface may be attributed to the reaction of CaO from Bakelite with Al_2O_3 from coke. The formation of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ at the interface

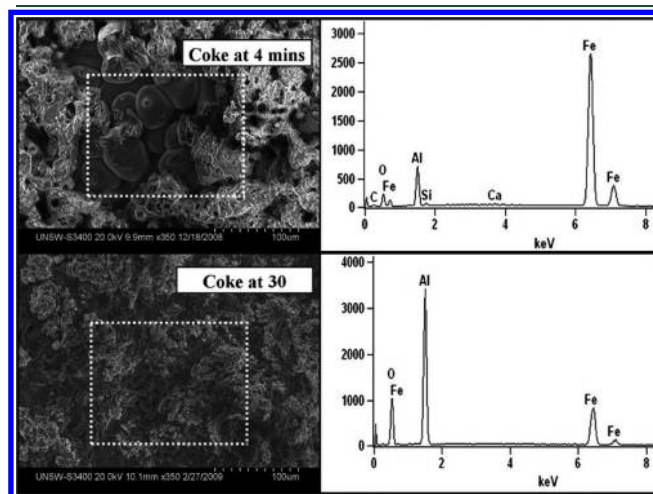


Figure 8. SEM images of the metal/carbon interface for coke and the EDS spectra of the interfacial region after 4 min of the carbon/metal interaction at 1550 °C.

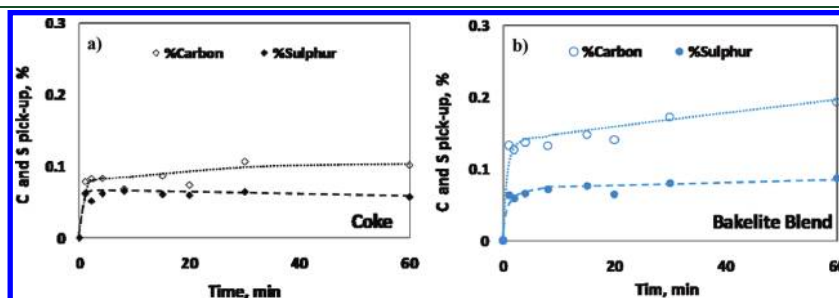


Figure 7. Carbon and sulfur picked up from (a) MC and (b) Bakelite/coke blend by liquid steel at 1550 °C.

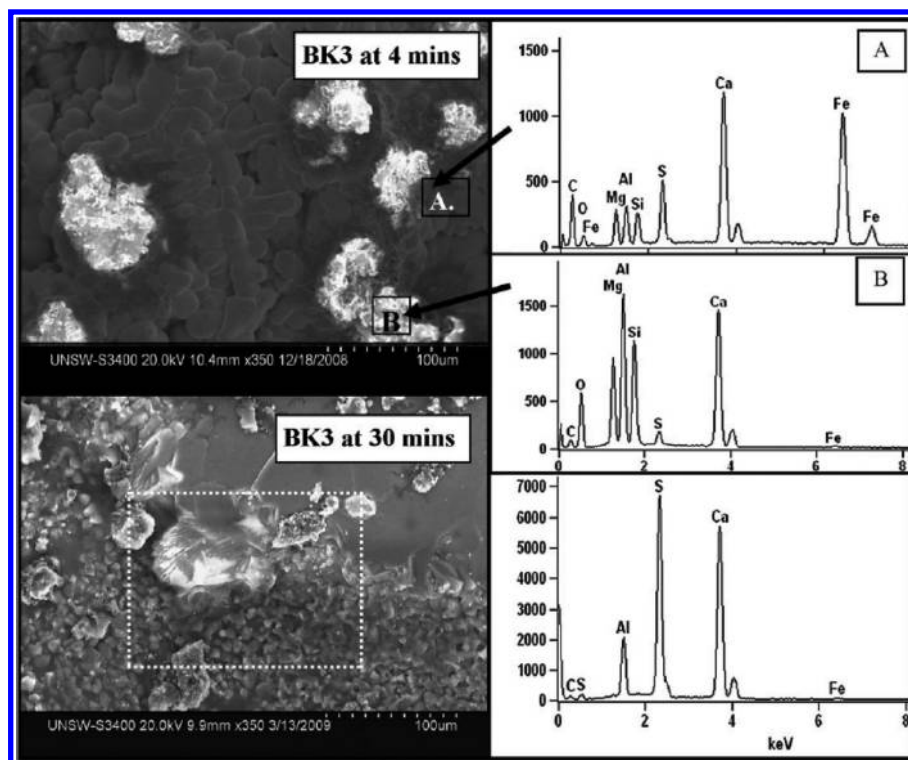
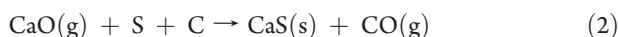
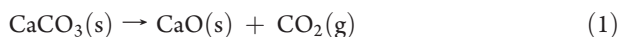


Figure 9. SEM images of the metal/Bakelite blend interface accompanied by EDS spectra of selected points of interest after 4 and 30 min of the carbon/metal interaction at 1550 °C.

was not seen in the case of coke alone, where the interface was predominately composed of Al_2O_3 .

The thermal decomposition of CaCO_3 into CaO takes place during the initial gas-phase reaction (reaction 1). As a result, the CaO content increases in the Bakelite/coke blend, thereby decreasing the Al_2O_3 content from the coke ash (see Table 3). Besides, CaO can help desulfurize the liquid metal through reactions with solute carbon and sulfur (reaction 2). This reaction transfers CaS to the metal/carbon interface as a reaction product.



Characteristics of the interfacial layer formed between the solid carbon and molten steel depends upon its fusion temperature, which, in turn, depends upon the chemistry of the layer.^{16,38} If the melting point of the ash layer is lower than the liquid metal temperature, it could be easily removed from the interface. This increases the contact area between the liquid metal and the solid carbon and, thus, enhances carbon dissolution. Orsten and Oeters³⁸ studied the influence of additives, such as CaO , on the carbon dissolution and found that the addition of CaO can reduce the ash melting temperature. It was concluded that the dissolution of coke was limited by the fusion temperature of ash.

In the present study, major components of the coke ash are SiO_2 and Al_2O_3 , while CaCO_3 is the key ash constituent when Bakelite is present. CaO obtained as a result of CaCO_3 decomposition may act as a fluxing agent, and this will reduce the ash melting temperature,³⁸ which, in turn, would increase the relative fluidity of the ash layer. The change in the properties of the ash layer would produce differences in carbon and sulfur pick-up

observed from Bakelite/coke blends. SiO_2 , Al_2O_3 , CaO , and MgO varied significantly across the Bakelite blends compared to its parent coke. The high CaO in the Bakelite/coke blend can decrease the melting temperature of the reaction products formed at the metal/carbon interface during reactions. FactSage 6.0⁴³ was previously employed²⁹ to estimate the proportion of the solid/liquid components of the interfacial products in the case of the coke and Bakelite blend at 1550 °C.

The constituents of the liquid component were found to be SiO_2 , Al_2O_3 , CaO , CaS , and Mg_2SiO_4 , while the major constituent of the solid component was $3\text{Al}_2\text{O}_3 \cdot \text{Si}_2\text{O}_{13}$ (mullite) and CaS . CaO and CaS at the interface are known to lower the melting temperature of the interfacial layer.

The liquid oxide layer, which is readily removed from the interface, can increase the metal/carbon contact area. These could explain the greater carbon pick-up values in the case of Bakelite/coke blends compared to coke alone. This provides the evidence that CaO generated from Bakelite has a beneficial effect in decreasing the ash fusion temperature of the materials, and this is in agreement with the results from the literature.³⁵

3.3.3. Influence of VM in the Polymer on Carbon Dissolution.

Raw HDPE was used as a carburizing material, and the carbon pick-up was measured after 2 and 60 min of reaction. The 100% HDPE transferred a significant amount of carbon in the liquid melt (2.48 wt %) compared to coke; the dissolution reaction took place in the first 2 min, after which just a marginal increase (2.65 wt %) in carbon pick-up was observed (Figure 10). The comparable values for 2 and 60 min (2.48 and 2.65 wt %, respectively) could be due to the fact that carburization of molten metal took place by carbon atoms released from volatiles that occurred in the first few minutes of the reaction. Afterward, the polymers were consumed, and no further carbon pick-up was observed.

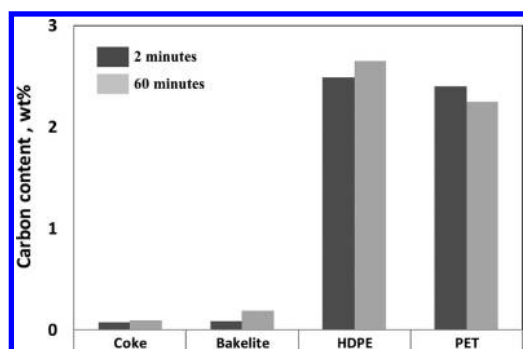


Figure 10. Comparison of carbon picked up after 2 and 60 min of reaction for coke, 100% Bakelite, 100% HDPE, and 100% PET.

Table 5. Percentage of the Oxygen Content in Liquid Steel after Reactions with the Coke and PET Blend at 1550 °C for Different Times^a

samples	percentage of oxygen in liquid steel		
	2 min	30 min	60 min
MC	0.0138 ± 0.0005	0.0480 ± 0.0032	0.0927 ± 0.0035
PET blend	0.0263 ± 0.0035	0.0550 ± 0.0037	0.0964 ± 0.0049

^aThe error is the standard deviation obtained for the duplicate runs of each sample.

The carbon pick-up from coke was ~0.1%, which was attributed to the composition and content of the ash present in coke, and thus, the interfacial products formed as a result of coke/metal reactions. When HDPE replaced coke, the carbon transfer into liquid metal was significantly higher. A high rate of devolatilization of HDPE plastics was reported to induce extra turbulence within the metal droplet³⁸ and, thus, produce a high mass transfer. This may have enhanced the carbon transfer, as seen in the case of HDPE compared to coke.^{39,40}

For coke, the mechanisms of carbon transfer are a dynamic balance between the exposure of the carbon surface to the melt

$$C_{\text{solid}} = C_{\text{liquid}} (\text{in Fe}) \quad (3)$$

and the physical barriers arising from either coke ash or melt-surface agents, such as sulfur.²¹

When plastics are introduced in the system, hydrocarbons (such as CH₄) and hydrogen are present and the carburization reaction is dictated via two parallel reactions (reactions 3 and 4).

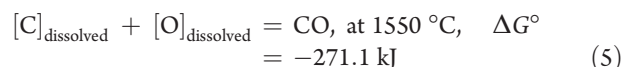


The rates of carburization were found to be significantly higher when CH₄ (5×)⁴¹ and especially hydrogen (16×)⁴² were present in the system. A study performed in ref 43 investigated the rate of carburization of liquid iron by CH₄ between 1400 and 1700 °C. The rate was measured for partial pressures of CH₄ in Ar in the range of 0.02–0.06 atm. Their results indicated that the rate of carburization is controlled by the dissociation of CH₄ on the liquid iron surface (reaction 4). The presence of H₂ was found to aid the carburization probably through the removal of adsorbed oxygen from the metal surfaces.

PET is quite different in structure and chemistry compared to the other plastics considered in the present study because it contains oxygen in its composition. Oxygen is expected to affect

the interfacial reactions, with liquid metal oxidizing the solute carbon in the melt. The carbon pick-up values from raw PET are relatively high compared to coke and are in the same range as the values observed for HDPE. The carbon pick-up value after 60 min was found to be slightly lower compared to that after 2 min, and this may be attributed to the presence of oxygen. The oxygen present in the polymer can react with carbon dissolved in liquid metal, thereby consuming a fraction of carbon.

PET contains high amounts of oxygen (Table 1). During carbon–metal interactions, oxygen diffusion into the liquid metal may occur. Solute carbon can be oxidized, generating CO, leading to depletion of solute carbon in liquid steel.



The oxygen content diffused in the metal droplets after the reaction with the coke and PET blend (see Figure 2) at different times was analyzed using an oxygen analyzer (LECO TC 436DR) (Table 5). It was found that oxygen levels in the metal droplets are far from the saturation limit.

The mass balance on carbon is conducted on a basis of unit mass of HDPE available for reaction (carbon dissolution and gasification). Some assumptions have been made to support the calculations, such that, at the studied temperature and under the conditions of the process (Ar and 1 L/min), the conversion of HDPE into hydrocarbons releases only methane (HDPE → CH₄ and CH₄ → C + 2H₂). Considering the fact that the mass of the iron chip used for carbon dissolution studies is 0.5 g and that the amount of carbon pick-up estimated in the iron is 2.48%, then 0.012 g of C released from HDPE was dissolved into liquid metal. The mass of HDPE used in the present study is 1.5 g. Assuming that only CH₄ is released at the studied temperatures, HDPE estimates an initial 1.28 g of carbon in its composition. On the basis of this assumption, we may conclude that approximately 1.27 g of carbon was gasified when HDPE reacted with the metal.

It was likely that oxygen in PET did not have much effect on oxidizing solute carbon in the melt. The improved performance over coke may be due to the presence of methane that was found to be quite considerable in PET.

The present study indicates that polymers could play an important role in carburization of molten metal, while their chemical and morphological structures play a key role. Among the polymers, Bakelite showed a much lower carbon pick-up compared to HDPE and PET, with a value comparable to coke. These finding can be explained in terms of the influence of volatiles (CH₄ and H₂) in HDPE and PET.

4. CONCLUSION

An in-depth investigation has been conducted on the usage of end-of-life polymeric materials for carbon/slag and carbon/metal reactions in the EAF steelmaking process. The major findings from this study are as follows: (1) The chemistry of the carbon-based material was seen to play an important role in the structure of the residual particle, influencing the release of gaseous emissions and, thus, the subsequent reactions with the slag. (2) An improvement in the slag volume ratios was observed when polymers substituted part of the coke. The rubber and PET blend showed an increased slag volume, in comparison to coke, allowing for the formation of stable foam throughout the experiment. The HDPE blend revealed significantly higher volume ratios as a result of increased gas generation, entrapment,

and subsequent release. (3) Gas bubbles were seen trapped within the slag matrix. Smaller bubble diameters were found when the polymeric materials replaced part of the coke, and such a result appears to be in good accordance with the estimated volume ratios. (4) Large differences in carbon pick-up values were found between coke and HDPE/PET. A marginal increase was seen when Bakelite represented the end-of-life plastic. Methane gas (from polymer decomposition) is responsible for the enhanced carbon pick-up values, increasing the rate of carburization to high extents. (5) The presence of CaCO_3 (present as a filler in Bakelite) transforms into CaO , which participates in desulfurization reactions to form CaS at the interface. The interfacial layer composition had been found to have an influence on the dissolution of carbon. (6) In this study, we have demonstrated that end-of-life polymers can be used as alternative carbon sources for slag and metal reactions in the EAF steelmaking process.

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REFERENCES

- Ogaki, Y.; Tomioka, K.; Watanabe, A.; Kuriyama, I.; Sugayoshi, T. *NKK Tech. Rev.* **2001**, 84, 1–7.
- Nakao, Y.; Yamamoto, K. *Nippon Steel Technical Report*; Nippon Steel Corporation: Tokyo, Japan, July 2002; Number 86, pp 21–24.
- Asanuma, M.; Ariyama, T.; Sato, M.; Murai, R.; Nonaka, T.; Okochi, I.; Tsukiji, H.; Nemoto, K. *ISIJ Int.* **2000**, 40, 244.
- Buchwalder, J.; Scheidig, K.; Schingnitz, M.; Schmöle, K. *ISIJ Int.* **2006**, 46 (12), 1767–1770.
- Ayed, P.; Clauzade, C.; Gros, B.; Huber, J.-C.; Lebrun, C.; Vassart, N. *Rev. Met. Paris* **2007**, 3, 128–135.
- Sahajwalla, V.; Rahman, M.; Khanna, R.; O’Kane, P.; Skidmore, C.; Knights, D. *Steel Res. Int.* **2009**, 80 (8), 531–539.
- Sahajwalla, V.; Khanna, R.; Zaharia, M.; Kongkarat, S.; Rahman, M.; Kim, B. C.; O’Kane, P.; Dicker, J.; Skidmore, C.; Knights, D. *Iron Steel Technol.* **2009**, 6, 43.
- Zaharia, M.; Sahajwalla, V.; Khanna, R.; Koshy, P.; O’Kane, P. *ISIJ Int.* **2009**, 49, 10.
- Sahajwalla, V.; Zaharia, M.; Rahman, M.; Khanna, R.; Saha-Chaudhury, N.; O’Kane, P.; Dicker, J.; Skidmore, C.; Knights, D. *Steel Res. Int.* **2011**, 81 (5), 566–572.
- Zaharia, M.; Sahajwalla, V.; Kim, B. C.; Khanna, R.; Saha-Chaudhury, N.; O’Kane, P.; Dicker, J.; Skidmore, C.; Knights, D. *Energy Fuels* **2009**, 23 (1), 89.
- Sahajwalla, V.; Zaharia, M.; Kongkarat, S.; Khanna, R.; O’Kane, P. *Energy Fuels* **2010**, 24 (1), 379–391.
- Hara, S.; Ogino, K. *ISIJ Int.* **1992**, 32 (1), 81–86.
- Olsson, R. G.; Koump, V.; Perzak, T. F. *Trans. Met. Soc. AIME* **1966**, 236, 426.
- Kosaka, M.; Minowa, S. *Trans. Iron Steel Inst. Jpn.* **1968**, 8, 392.
- Mourao, M. B.; Murthy, G. K.; Elliott, J. F. *Metall. Trans. B* **1993**, 24, 629.
- Gudenau, H. W.; Mulanza, J. P.; Sharma, D. G. R. *Steel Res.* **1990**, 61, 97.
- Jones, N. W. *Ironmaking Steelmaking* **1998**, 25, 460.
- Shigeno, Y.; Tokuda, M.; Ohtani, M. *Trans. JOM* **1985**, 26, 33.
- Wu, C.; Sahajwalla, V. *Metall. Trans. B* **2000**, 31B, 243.
- Wright, J. K.; Baldock, B. R. *Metall. Trans. B* **1988**, 19, 375.
- Ericsson, S. O.; Mellberg, P. O. *Scand. J. Metall.* **1981**, 10, 15.
- Sahajwalla, V.; Khanna, R. *Metall. Trans. B* **2000**, 31, 1517.
- Khanna, R.; McCarthy, F.; Sun, H.; Simento, N.; Sahajwalla, V. *Metal. Trans. B* **2005**, 36, 719.
- Cham, S. T.; Sahajwalla, V.; Sakurovs, R.; Sun, H.; Dubikova, M. *ISIJ Int.* **2004**, 44, 1835.
- McCarthy, F.; Sahajwalla, V.; Hart, J.; Saha-Chaudhury, N. *Metall. Mater. Trans. B* **2003**, 34, 573.
- Wu, C.; Wiblen, R.; Sahajwalla, V. *Metall. Mater. Trans. B* **2000**, 31, 1099.
- Zhao, L.; Sahajwalla, V. *ISIJ Int.* **2003**, 43, 1.
- McCarthy, F.; Khanna, R.; Sahajwalla, V.; Simento, N. *ISIJ Int.* **2005**, 45, 1261.
- Khanna, R.; Rahman, M.; Leow, R.; Sahajwalla, V. *Metall. Trans. B* **2007**, 38, 719.
- Kongkarat, S.; Khanna, R.; Koshy, P.; O’Kane, P.; Sahajwalla, V. *Steel Res. Int.* **2011**, DOI: 10.1002/srin.201100104.
- Dankwah, J. R.; Koshy, P.; Saha-Chaudhury, N.; O’Kane, P.; Skidmore, C.; Knights, D.; Sahajwalla, V. *ISIJ Int.* **2011**, 51 (3), 498–507.
- Sahajwalla, V.; Zaharia, M.; Kongkarat, S.; Khanna, R.; Saha-Chaudhury, N.; O’Kane, P.; Skidmore, C.; Dicker, J.; Knights, D. *Proceedings of COM 2011*; Canada, 2011.
- Katayama, H.; Taguchi, S.; Tsuchiya, N. *Trans. Iron Steel Inst. Jpn.* **1982**, 68 (15), 2279–2286.
- Nagasaka, T.; Hino, M.; Ban-Ya, S. *Metall. Mater. Trans. B* **2001**, 31 (5), 945–955.
- Zhang, Y.; Fruehan, R. J. *Metall. Mater. Trans. B* **1995**, 26, 813–819.
- Ogawa, Y.; Katayama, H.; Hirata, H.; Tokumitsu, M.; Yamau-chi, M. *ISIJ Int.* **1992**, 32 (1), 87–94.
- Cham, S. T.; Khanna, R.; Sahajwalla, V.; Sakurovs, R.; French, D. *ISIJ Int.* **2009**, 49, 1860.
- Orsten, S.; Oeters, F. *Process Technology Conference Proceedings, Institute for Scientific Information*; Philadelphia, PA, 1986; Book 3, p 143.
- Barin, I.; Modigell, M.; Safert, F. *Metall. Trans. B* **1987**, 18, 347–354.
- Sohn, I.; Fruehan, R. J. *Metall. Mater. Trans. B* **2005**, 36, 605.
- Sekino, K.; Nagasaka, T.; Fruehan, R. J. *Metall. Mater. Trans. B* **1995**, 26, 317–324.
- Kim, K. S.; Seo, J. H.; Nam, J. S.; Ju, W. T.; Hong, S. H. *IEEE Trans. Sci.* **2005**, 33 (2), 813–823.
- Bale, C. W.; Pelton, A. D.; Thompson, W. T.; Eriksson, G.; Hack, K.; Chartrand, G.; Decterov, S.; Melancon, J.; Petreson, S. *FactSage 6.0*; GTT Technology: Aachen, Germany, 2009.