Recycling of End-of-Life Polycarbonate as a Carbon Resource in Ironmaking*

[1]E. Abotar and [1]J. R. Dankwah
[1]University of Mines and Technology, Tarkwa, Ghana

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Abstract

Globally, millions of end-of-life Polycarbonates (PC) are generated annually. Landfill disposal is one of the primary options for handling end-of-life PCs. There is a possible potential release of Bisphenol-A (BPA) from PC via hydrolysis or leaching when disposed at landfill sites. In this work the use of end-of-life PC as reductant for the production of metallic iron from Mbalam iron oxide was investigated in a horizontal tube furnace through the composite pellet approach. Elemental analysis of the charred PC shows a carbon content of (78.92 wt %) and hydrogen content of (7.07 wt %) which are reasonably above those of various forms of coals and can be recovered for use as reductant in metal extraction processes. Composite pellets of high-grade Mbalam iron ore (assaying ~97 % Fe_2O_3) with charred end-of-life PC were heated from room temperature to 800 °C and then between 800-1300 °C in a continuous stream of pure argon and the off gas was analysed continuously using an infrared (IR) gas analyser. Elemental analyses of samples of the reduced metal were performed chemically for its oxygen content using a LECO oxygen/nitrogen analyser. Gas emission studies revealed the emission of large volumes of the reductant gas CO along with CO_2. It is further demonstrated that end-of-life PC is effective in reducing iron oxide to produce metallic iron with reduction in oxygen content from 30.99 wt % to 0.0372 wt % corresponding to 99.88 % in less than 2400 s.

Keywords: Polycarbonate, Extent of reduction, Bisphenol A, Infrared gas Analyser, LECO Carbon/Sulphur Analyser

1 Introduction

Globally, millions of end-of-life Polycarbonates (PC) are generated annually. Major avenues available for dealing with end-of-life PC are disposal at landfill sites and incineration. It is difficult to recycle this category of plastics because they are produced from thermosetting polymers and cannot be remoulded after setting (Dankwah *et al.*, 2016). Conventional methods for recycling PC have concentrated largely on disposal at landfill sites. Decreasing landfill space along with increasing landfill costs call for novel ways for recycling of PC.

There is a possible potential release of Bisphenol-A from PC into water bodies via hydrolysis or leaching when disposed at landfill sites. BPA is one of the endocrine-disrupting chemicals that are ubiquitous in aquatic environments (Yang *et al.*, 2015).

The technology of reduction using end-of-life polymers is an emerging area in Metallurgy where carbonaceous materials generated from end-of-life polymers are used as reductants for metal oxides reduction (Abotar *et al.*, 2020).

For countries like Cameroon where commercial quantities of iron ores are available, but without the relevant source of carbonaceous materials, end-of-life polymers offer a readily available alternative to high grade metallurgical coke as reductant for iron making. In the metallurgical field, the use of postconsumer plastics as reductants or as a source of energy is currently gaining the attention of various researchers (Matsuda *et al*., 2006; Nishioka *et al*., 2007; Matsuda *et al*., 2008; Ueki *et al*., 2008; Dankwah *et al*., 2011; Kongkarat *et al*., 2011; Murakami *et al.*, 2009; Murakami and Kasai, 2011; Dankwah *et al*., 2012; Dankwah and Koshy, 2014). However, most of the existing research in this area involves the use of thermoplastic polymers and or their blends with metallurgical coke, graphite, or biomass as reductants for the production of metallic iron from reagent grade iron oxides.

Rajarao *et al*., (2014b) for instance studied the structural changes in the chars produced during the rapid pyrolysis of waste compact discs (CDs) in the temperature range 550-1550 °C. They observed that the porosity and C/O ratios of the chars increased with an increase in the pyrolysis temperature up to 850 °C. Maximum porosity was achieved at 850 °C with char surface area of 334 m^2/g using the chars produced at 1550 °C as reductants, they were able to achieve about 90% iron oxide reduction.

For thermosetting polymers and elastomers, Abotar *et al.*, 2020, Dankwah *et al*., 2012, Mansuri *et al*., 2013, Rajarao *et al*., 2014a, Rajarao *et al*., 2014b, Nath *et al*., 2012, Dhunna *et al*., 2014, Dankwah and Baawuah, 2015 and Dankwah *et al.*, 2016; have used end-of-life rubber tyres, waste compact discs, end-of-life melamine, waste bakelite, end-of-life electrical sockets as reductants for the carbothermal reduction of iron ores.

More information is needed in the literature on the use of PC as reductants for the production of metallic iron from naturally occurring iron ores. Besides, the use of Polycarbonate as reductants for metal production has not been well studied.

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2 Resources and Methods Used

2.1 Materials

A quantified amount of end-of-life PC was collected from Tarkwa. These were broken into pieces and rinsed with ethanol in a plastic container to remove most of its associated debris. The cleaned PC were thereafter air dried for two days. Charring was done under controlled temperature conditions to upgrade the carbon content by expelling the volatile components of the material. The residence time of the charring process was 20 min using a gas fired furnace. The charred PC was ground using a ball mill for 10 minutes. The ground PC was screened using a standard sieve size of 125 μm as shown in Fig 1. High grade Mbalam iron ore (96.56 wt % Fe2O3) obtained from Cameroun was used as the source of iron oxide (Table 1). The morphology of the Mbalam iron ore was observed by Scanning Electron Microscopy (SEM) as shown in Fig 2. The pulverised samples were characterised by XRD using an EMPYREAN Diffractometer

Table 1 Elemental Analysis of Mbalam Iron Ore

Component	Composition (wt%)
Na_2O	0.05
Al_2O_3	0.46
SiO_2	0.46
P_2O_5	0.12
Fe_2O_3	96.56
CuO	0.01
ZnO	0.03
BaO	0.01
L.O.I.	0.41

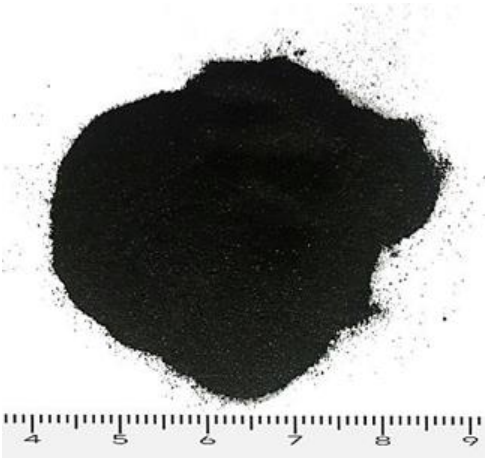


Fig. 1 Pulverised Sample of Charred End-of-life PC

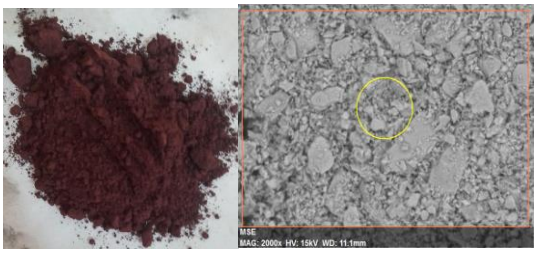


Fig. 2 a) Photo and b) SEM Photomicrograph of Pulverised Mbalam Iron Ore utilised for the Studies

2.2 Reduction Studies

Cylindrical pellets were formed from pulverised Mbalam iron oxide and pulverised charred polycarbonate (~ 30 wt %) with about 2 wt % flour as binder and appropriate amount of water (Fig. 3). After curing and drying for 96 hours the composite pellets were then ready for firing in a resistance heated horizontal tube furnace (Fig. 4). The furnace was purged continuously with argon gas (99.995% purity) to ensure an inert atmosphere. The furnace was preheated to a desired temperature of 800 °C and the sample was inserted; gas measurement commenced immediately after insertion and continued for 2400 s. No appreciable change in gas composition was observed beyond 2400 s. Reacted carbonaceous material/iron oxide samples were quenched by rapidly withdrawing the tray from the hot zone into the cold zone of the furnace. Particles of reduced iron metal, which were clearly visible to the naked eye, were removed by a magnetic screw driver and its oxygen content was determined by LECO Nitrogen/Oxygen analyser (model TC-436 DR 602-500-600, LECO Corporation, Michigan, USA).

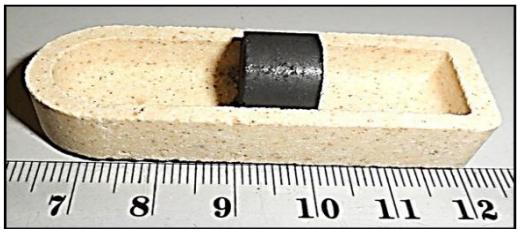


Fig. 3 Cylindrical Pellet of Fe_2O_3-PC Composite in a LECO Crucible

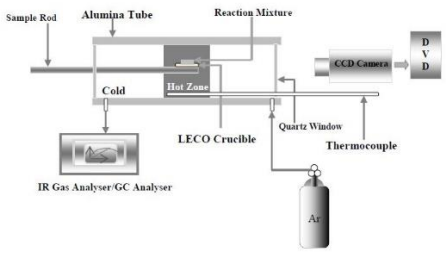


Fig. 4 Schematic of Horizontal Tube Furnace used for Reduction Studies

3 Results and Discussion

3.1 Charred PC

Fig. 5 shows the elemental analysis of the solid product obtained after charring PC. Elemental analysis of the charred PC shows a carbon content (of 78.92 wt %) reasonably above those of various forms of coals (~60 wt %) and polyethylene terephthalate (PET) (~62.5 wt %).

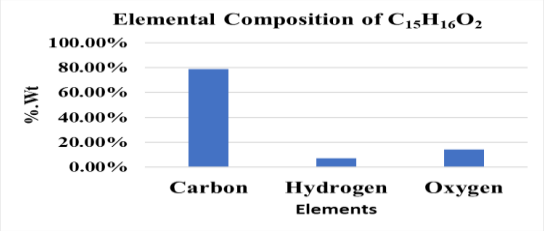


Fig. 5 Elemental Analysis of Charred PC

3.2 Nature of the Mbalam Iron Ore

The ore was also characterised by XRD. The diffraction patterns are shown in Fig. 6. and consist of several crystalline peaks of Fe_2O_3.

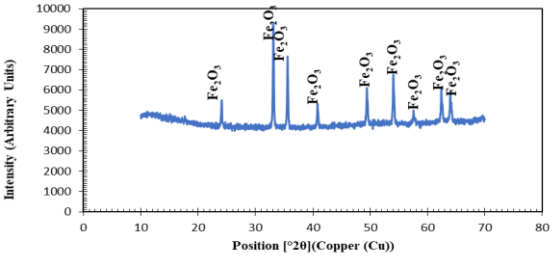


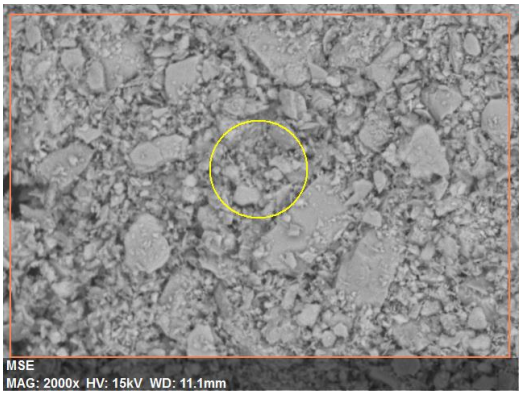
Fig. 6 XRD of Mbalam Iron Ore

The SEM/EDs analyses of the Mbalam iron ore as showed in Fig. 7 and Table 3 indicates an Fe content of 65.67 wt%. Comparing the chemical composition of Mbalam iron ores to the commercial chemical composition requirement of various ironmaking process routes in Table 2, it is seen that the Mbalam iron ores fall in all the various process routes.

Table 2 Commercial Requirement for Various Ironmaking Process Routes

Process	Minimum Fe (wt %)	Maximum Gangue (%) (SiO2 + Al2O3)	LOI (%)
Corex	65.0	4.0	-
BF	62.0	6.0	2.0
Midrex (DRI)	67.0	3.2	1.5
HYL (DRI)	65.5	2.2	1.5
Rotary Kiln (DRI)	64.0	4.0	-

(Source: Lu, 2015)



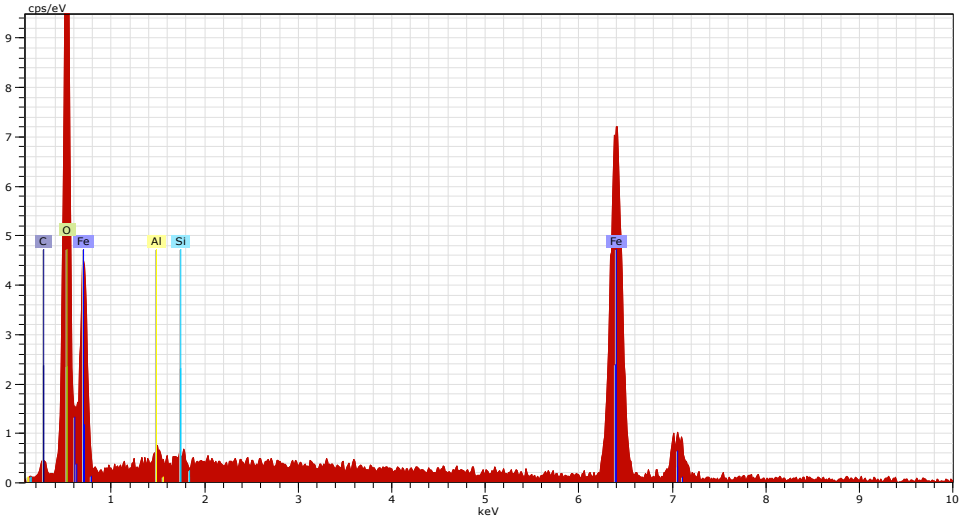


Fig. 7 SEM/EDs Analysis for Mbalam Iron Ore

Table 3 Values of SEM/EDs Analysis for Mbalam Iron Ore

Element (K series)	Weight %	Atomic %
F	65.67	35.14
O	30.99	57.87
C	2.40	5.97
Si	0.33	0.35
Al	0.61	0.67
SUM	**100**	**100**

3.3 Reduction Studies

3.3.1 Gas Generation Behaviour during Heating of Fe_2O_3-PC Composite Pellet

The gas Generation behaviour during Heating of Fe_2O_3-PC composite pellet is illustrated in Fig 8. The major component of the off gas is CO with a maximum concentration of about 9.9 vol %, some CO_2 is also observed with a maximum concentration of 1.7 vol %. The potential for PC to function as a reductant for iron oxide reduction therefore exists, as indicated by the formation of CO gas. An increase in the reduction time increases the temperature which appears to have a very significant effect on gas generation, especially CO as illustrated in Fig. 8. The concentration of CO increased from about 0.6 vol % at 140 s to about 9.9 vol % at 280 s, implying that reduction (removal of oxygen) is influenced by temperature as the time is increased. The effect of temperature on CO_2 is rather the reverse of what was observed for CO, judging from the area under the graphs of CO_2 in Fig. 8. This is explained by the consumption of CO_2 by solid carbon through the highly endothermic Boudouard reaction Eq. 1 which is favored at high temperatures (Knacke *et al.,* 1991 and Dankwah and Buah 2017):

$$CO_2 + C = 2CO$$

$$\Delta G = +170700 - 174.5T\,J \qquad (1)$$

Another possible reaction that could contribute to the observed surge in the concentration of CO at 280 s is the water gas reaction illustrated in Eq. 2 (Knacke *et al.,* 1991 and Dankwah and Buah, 2017)

$$H_2O + C = H_2 + CO$$

$$\Delta G = +134700 - 142.5T\,J \qquad (2)$$

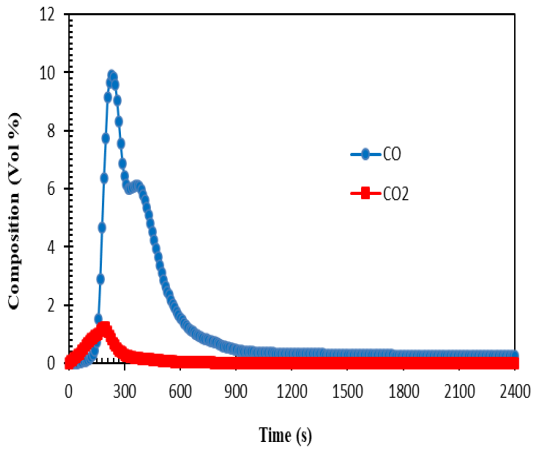


Fig. 8 Gas Generation Behaviour during Heating of Fe_2O_3-PC Composite at 1250 °C

The accumulated amount of gases evolved (nCO and nCO_2) are shown in Fig 9. This shows that an increase in time leads to an increase in the amount of CO and a decrease in the amount of CO_2 produced

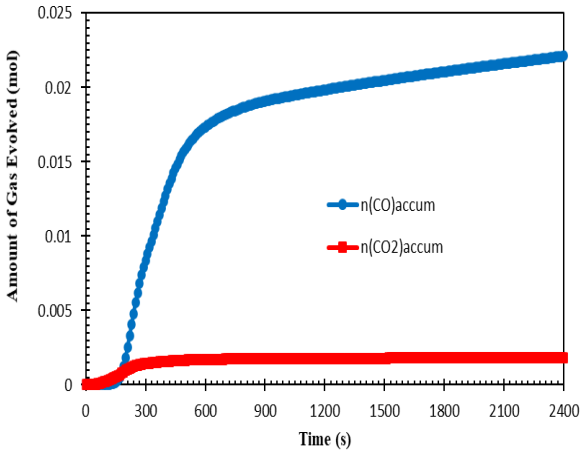


Fig. 9 Accumulated Amount of Gas Generated at 1250 °C

Possible reactions for the reduction of Fe_2O_3 to Fe are:

$$Fe_2O_3 + 3C = 2Fe + 3CO \qquad (3)$$
$$Fe_2O_3 + 3CO = 2Fe + 3CO_2 \qquad (4)$$
$$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O \qquad (5)$$

3.3.2 Extent of Reduction

The extent of reduction was calculated from the oxygen content of the reduced metal produced from the reaction of the iron oxide with PC. The result is shown in Fig. 10 for reduction at 2400 s. PC is able to reduce Fe_2O_3, attaining a complete reduction in less than 2100 s.

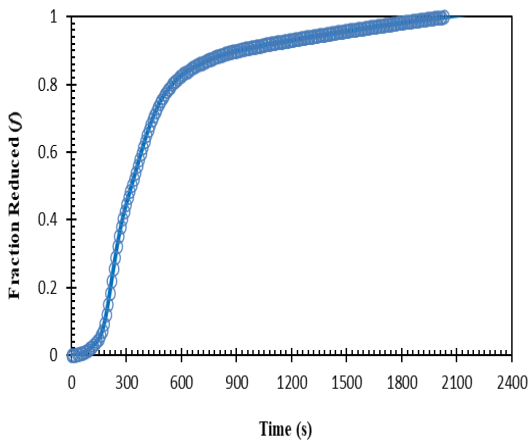


Fig. 10 Variation of Fraction Reduced with Time

3.4 Nature of Metals Produced

Spherical metals produced. The spherical nature of the reduced iron metal is attributed to the excess carbon present in the iron ore-carbon composite causing the reduced iron to pick up these excess carbons causing the reduced iron to melt at a lower temperature into a molten mass that solidifies into sphere when the tray had been withdrawn from the reaction zone to the cold zone. A clear separation of reduced metal from the slag layer was observed at a 1250 °C, as shown in Fig. 11. LECO O/N analyser revealed a reduction in oxygen content from 30.99 wt % to 0.0372 wt % corresponding to 99.88 % reduction.

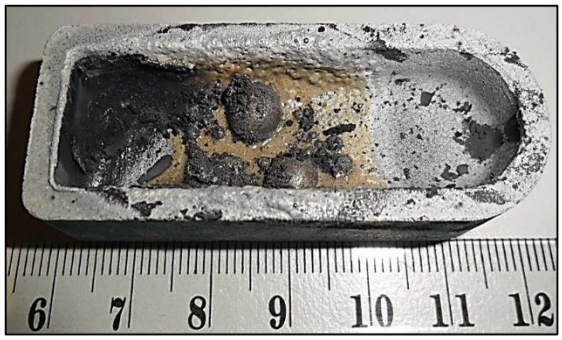


Fig. 11 Droplets of Metallic Iron obtained after Reduction of Fe_2O_3-PC Composite at 1250 °C

The XRDs of the raw Fe_2O_3 and the clearly separated reduced metal are shown in Figs 6 and 12, respectively. The sharp peaks of Fe_2O_3 in Fig 6 are observed to disappear completely after reduction and are replaced by sharp peaks that correspond to Fe and Fe_3C in Fig 12. End-of-Life PC is therefore able to reduce Fe_2O_3 to produce highly carburised metallic iron.

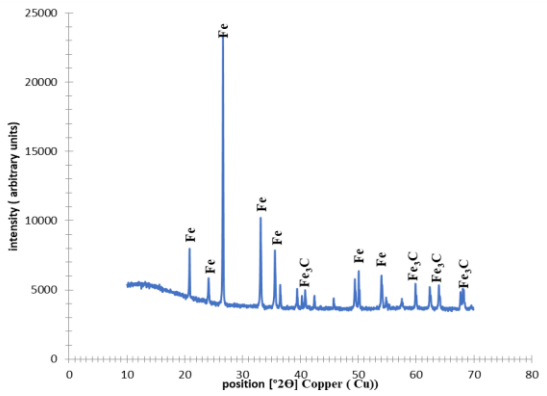


Fig. 12 XRD of Reduced Pellets of Fe_2O_3-PC Composite Pellets

4 Conclusion

The reduction of iron oxide (Fe_2O_3) has been investigated using carbonaceous material prepared from end-of-life PC as reductant. Major findings of the investigation are:

i. Thermal decomposition studies revealed the generation of large volumes of the reductant gas CO, indicating the potential of end-of-life PC as a reductant in ironmaking;

ii. Metallic iron was produced after heating Fe_2O_3-PC composite;

iii. Slag-metal separation improved with temperature, with complete slag-metal separation being attained at 1250 °C.

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Authors

Emmanuel Abotar is a Lecturer and a PhD candidate at the Minerals Engineering Department of the University of Mines and Technology, (UMaT), Tarkwa. He obtained his MPhil and BSc Degrees in Minerals Engineering at the University of Mines and Technology. His current research areas include Mineral processing, iron and steelmaking, high-temperature metallurgical processes and utilisation of waste polymers in metal extraction processes

James R. Dankwah is an Associate Professor and Dean of the Faculty of Integrated and Management Studies at the University of Mines and Technology, UMaT-Tarkwa. He obtained his PhD from the School of Materials Science and Engineering, UNSW-Australia, MSc (Process Metallurgy) from the Norwegian University of Science and Technology and BSc (Metallurgical Engineering) from the Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. His current research areas include iron and steelmaking, high-temperature metallurgical processes, utilisation of waste polymers in metal extraction processes and recycling agricultural waste into building blocks materials for affordable housing for the rural folks. He is a Fellow of the West African Institute of Mining, Metallurgy and Petroleum (WAIMM).