

Simultaneous Production of Metallic Iron and Syngas from EAF slags using Waste Plastic Sachet Bags as a Reducing Agent

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Abstract

Global environmental legislation on the disposal of waste materials has increased the need for novel process technologies that will create values from these waste materials. The present investigation is aimed at feasibility studies on the production of metallic iron and syngas from EAF slags using waste plastics sachet bags as reducing agent. Mixtures of waste plastics sachet bags and waste EAF slags were heated very rapidly in a laboratory scale horizontal tube furnace between 1700 and 1800 K in a continuous stream of ultrapure argon. Reaction products, which consisted predominantly of metallic iron, char, syngas ($\text{CO} + \text{H}_2$), and minor amounts of CO_2 , H_2O and CH_4 were analysed and detected using an IR gas analyser, gas chromatography and chemical analysis. The results indicated that it is possible to produce metallic iron and syngas with virtually no production of CO_2 and that the hydrogen portion of the waste plastics is the predominant reductant in the first ten minutes of the reduction process.

1 Introduction

The exploitation of the Opon Mansi iron ore deposit and the subsequent establishment of an integrated Iron and Steel Mill have been on the drawing boards of successive governments. The lack of progress on the establishment of an iron and steel mill may be due to the 'absence' of an appropriate source of coal/coke, which is the conventional reductant used for ironmaking and steelmaking. There is therefore the need to look for other appropriate materials that can chemically perform the same function as coke. Production of charcoal by cutting down trees would not be appropriate at a time when the Country is faced with the huge problem of deforestation. Potential materials that could replace coke, in this respect, include waste biomass (sawdust, coconut and palm nut shells) and waste plastics materials.

The world's annual consumption rate of plastic materials has increased from around 5 million tonnes in the 1950's to nearly 100 million tonnes today (recycling survey, 2005). In Ghana there are 895 plastic manufacturing companies and sachet water producers that churn out about 26,000 metric tonnes of plastic products annually. Over the years, plastics have replaced leaves, glass and metals as a cheaper and more efficient means of packaging (IRIN, 2006). However, the reckless disposal of these plastics, which are non-biodegradable, has contributed in the choking of drains and polluting of our beaches. The scourge of the plastic waste seems to have grown out of hand and overwhelmed the various Municipal, Metropolitan and District Assemblies. Official estimates from the Accra Metropolitan Authority (AMA) indicate that about 270 tonnes of plastic waste are generated each day in Accra alone (IRIN, 2004). The most common type of plastic waste within the municipal waste stream is the "sachet" water film bags that are discarded indiscriminately soon after consuming its contents (Wienaaah, 2005) and these water sachets are believed to account for about 85 percent of this category of waste (IRIN, 2004). Figures from the waste management division (WMD) of AMA indicate that only 2 percent of the plastics waste generated is recycled (Anomanyo, 2004)

However, sustainable development demands an environmentally and economically sound mode of disposal of these waste materials, especially those that are not biodegradable.

Globally, the main options available for the disposal of waste plastics are landfills, incineration, and recycling. However, the recycling option is limited, as only 7% of plastics are recycled (Environment Agency of UK, 2001) and the conventional way of recycling is known to be uneconomical and labour intensive. Landfill and incineration are not environmentally viable options either, as toxic and environmentally unfriendly gases are known to evolve at landfill sites. The production of these gases contributes to the overall emission levels of toxic methane and carbon dioxide to the environment. There is also the problem of leaching of toxic chemicals into the surrounding bedrock. Again, during incineration processes, hazardous air pollutants such as dioxins, furans and polycyclic aromatic hydrocarbons (PAHs) are produced (Li et al, 2001)

There is a limit to the number of times this category of waste stream could be recycled mechanically, after which they must be discarded or recycled by other means.

In the present work, the production of metallic iron and syngas from EAF slags containing FeO using waste 'pure water' plastic sachet bags was investigated under inert atmosphere in a custom

made horizontal tube furnace. The events taking place during the reduction process were identified and kinetic data were captured to fit the reduction data.

1.1 Plastic Material Used for Sachet-water Production

The bags used for packaging factory produced sachet water are made of high-density polyethylene (HDPE), [Okiogah, 2005] which has the repeating unit - $[\text{CH}_2\text{-CH}_2]$ - and a density that ranges from 0.940 to 0.970 g/cm^3 . HDPE is a semi-crystalline polymer with a very high crystallinity and consists of molecules that are characterized by an extremely long carbon backbone with virtually no branching.

As a material resource for iron and steel making, HDPE contains both carbon and hydrogen and can undergo gasification under such conditions to produce CO and H₂, which are needed for the reduction of iron oxide. As a source of energy, HDPE is a store of vast chemical energy and has a calorific value comparable to that of diesel oil (Table 1); its usage in EAF steelmaking process results in lower energy consumption that has been attributed to better slag foaming (Sahajwalla et al 2006, Rahman et al 2006, Sahajwalla et al 2007).

One of the cardinal reasons that account for the shift from the traditional coke-based blast furnace process of ironmaking to modern processes such as natural gas-based (Midrex, HYL, FINMET) and coal-based (Fastmet, Primus, ITmk3) has been the need to address the huge environmental concerns often raised by the various EPAs of countries involved in or hoping to embark on iron and steel making. However, the price of natural gas has risen consistently in the past decade compared to relatively steady prices of coal. The carbon composite method [Matsui et al. (2003), Kasai et al., (2003), Nakano (2004) and Sun and Lu (1999)], which uses a briquette mixture of iron ores and coals enhances the reaction rate considerably and the method is also expected reduce CO₂ emissions in the ironmaking process (Ueki et al., 2008). However, coal and natural gas are not sustainable in the long term as fossil fuels and the burning of coal causes environmental problems (greenhouse gases). Waste plastics can be utilised (as an alternative to coal or in blends with coal) as a reductant and source of chemical energy in the carbon composite method to reduce CO₂ emissions further, since it contains a huge amount of H₂.

Table 1 Locked-in potential (LIP) expressed as calorific value for a range of materials

Product	Energy
Polymer	LIP (MJ/kg)
Polypropylene	46
Polyethylene (HDPE, LDPE)	46
Polystyrene	41
Polyurethane	24-31
Polyester	19-30
PVC	20
Conventional Fuels	Energy (MJ/kg)
Diesel Oil	46
Naphtha	42-46
Carbon	21-33
Wood	16-21
Paper	16-19

Source: Horrocks, R., 1996

1.2 Previous Research and Developments

The utilisation of waste plastics as supplementary fuel with coke and coal has generated tremendous interest in recent years, culminating in the development of innovative technologies in this field. Notable developments include the commercial utilisation of waste plastics in the power industry and as fuel in blast furnaces (JFE & Nippon steel, Japan and Bremen steel works, Germany) [Sahajwalla et al, 2008; Yeo, 1997; Janz and Weiss, 1996; Yoshitsugu, 2003]. Asanuma et al, 2000 have investigated the use of waste plastics as coal-plastic mixtures in NKK Keihin's blast furnace. They observed that plastics had higher combustion and gasification efficiencies compared with pulverized coal and concluded that waste plastics could be effectively utilized both as a reducing agent and as a source of fuel in blast furnaces. As plastics generally have higher hydrogen content than coke/coal, these could also help reduce overall CO₂ gas emissions. Ariyama et al, 1997 have reported that, pulverized coal and waste plastics could be effectively used to melt scrap steel and these fuels could be injected into the furnace through the oxygen nozzle. Tadashi, 2005 has investigated the use of waste plastics as a source of carbon in

EAF steelmaking using a mass-production furnace and has confirmed a decrease in the electrical power consumption and increasing carbon levels in the steel melt. Dankwah et al. (2010) investigated the reduction of FeO in EAF steelmaking slag by metallurgical coke and waste plastics blends. They reported significant improvements in rates and percentage reduction when the metallurgical coke was partly blended with HDPE, and attributed the improvements in rate of reduction to the release of H₂ gas from the HDPE. However, only few studies (Ueki et al., 2008, Nishioka et al., 2007, Hasegawa et al., 2003, Hasegawa et al., 2004 and Matsuda et al., 2006) exist in the literature on the utilisation of waste plastics as a reductant in the carbon composite method.

1.3 Relevant theory

Each of the slag-plastics pellets behaves as a micro-reactor in the horizontal tube furnace. During the heating process, the polymeric reductant contained in a pellet decomposes and the decomposition products of this organic material are believed to reduce the iron oxide to metallic iron.

The reactions that are believed to occur at steelmaking temperatures are divided into the following four categories:

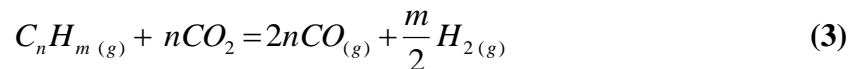
1) Conversion of polymers into hydrocarbons (mainly CH₄)



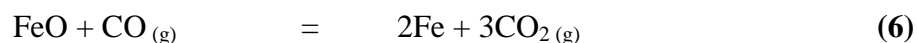
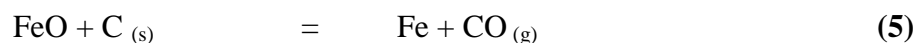
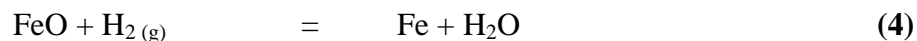
2) Decomposition of hydrocarbons into carbon (which is deposited in the pellet) and hydrogen (which can give rise to reduction or escape from the pellet):



The hydrocarbon could also act as a sink for CO₂ gas, producing CO and H₂ (equation 3)

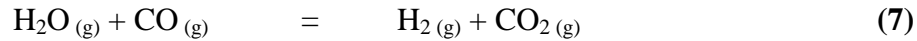


3) Reduction of iron oxide by hydrogen, carbon and carbon monoxide:

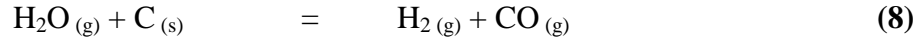


4) Auxiliary reactions [Gosh et al, 1986]

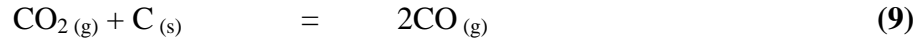
i) Water gas shift reaction:



ii) Reaction of water vapour with C produced from cracking of C_nH_m :



iii) Boudouard reaction:



iv) Carbon dissolution into molten metal:

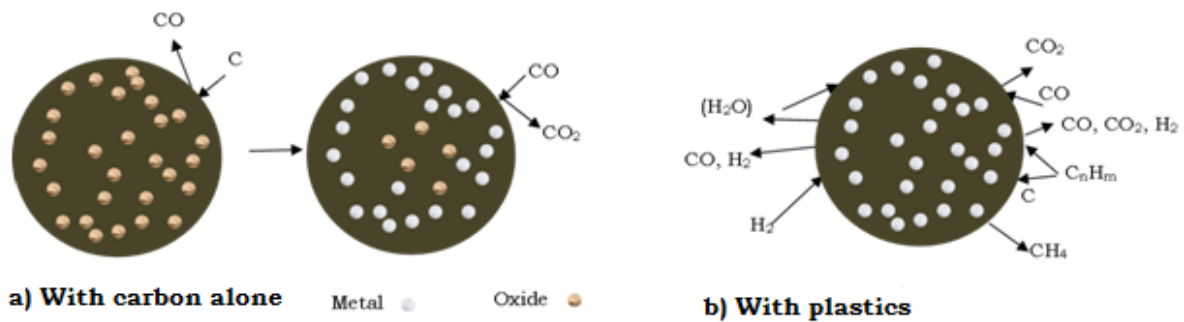


Figure 1: Schematic illustration for (a) iron oxide – carbon reaction and (b) the enhanced reaction of FeO in the presence of hydrocarbons generated from plastics

1.4 Calculation of rate and extent of reaction

The off gas data (CO and CO_2) were generated continuously from an IR. Thus the overall rate of gas generation could be described as a continuous function R_o which is a function of time. The extent of reduction can be estimated by integrating R_o according to the equation:

$$P = \frac{1}{N_o} \int_0^t R_o \cdot dt \quad (11)$$

Where: N_o is the total amount of reducible oxygen in the slag.

R_o was estimated from the individual molar fluxes, J_i , ($\text{mol cm}^{-2} \text{ s}^{-1}$) as shown in the equation below:

$$R_o = J_{CO} + J_{H_2O} + 2.J_{CO_2} = -J_{FeO} \quad (12)$$

Assuming that the gases behave ideally, the flux of CO, CO₂, H₂ and H₂O can be represented by the following equation (room temperature = 20°C).

$$J_i = \frac{273}{293} \times F_{Ar} \times \frac{\% i}{22.4 \times \% Ar} \cdot \frac{1}{A} \quad (13)$$

The rate of FeO reduction is thus given by the expression

$$rate = -\frac{1}{A} \frac{d(n_{FeO})_t}{dt} = -J_{FeO} \quad (14)$$

$$rate = \frac{0.0416}{A} \times F_{Ar} \times \left(\frac{2 \times \% CO_2 + \% CO + \% H_2O}{\% Ar} \right) \quad \text{mol cm}^{-2} \text{ s}^{-1} \quad (15)$$

Where: J_i , n_{FeO} , F_{Ar} and A are the molar flux (mol of species i/cm²sec), amount of FeO (mol) at time t, Ar flow rate (F_{Ar} =1L/min) and reaction area (cm²) respectively.

1.5 Reaction rate constants

The mass of FeO (m_{FeO}) in the slag can be calculated from the relation

$$\begin{aligned} (\% FeO) &= \frac{m_{FeO}}{W_{slag}} \times 100 \\ &= \frac{M_{FeO} \cdot n_{FeO}}{W_{slag}} \times 100 \end{aligned}$$

The amount of FeO (n_{FeO}) in the slag can thus be written as

$$n_{FeO} = \frac{(\% FeO) \cdot W_{slag}}{100 \times M_{FeO}}$$

The rate of reduction of FeO in the slag is given by the expression

$$rate = -\frac{1}{A} \cdot \frac{d(n_{FeO})}{dt} = -\frac{W_{slag}}{100 \cdot A \cdot M_{FeO}} \cdot \frac{d(\% FeO)}{dt}$$

Assuming a first order rate law

$$rate = -\frac{1}{A} \cdot \frac{d(n_{FeO})}{dt} = k \cdot (\% FeO) = -\frac{W_{slag}}{100 \cdot A \cdot M_{FeO}} \cdot \frac{d(\% FeO)}{dt}$$

$$\frac{d(\%FeO)}{dt} = -\frac{100.k.A.M_{FeO}}{W_{slag}}.(\%FeO)$$

By integrating,

$$\ln\left\{\frac{(\%FeO)}{(\%FeO)_o}\right\} = -\frac{100.M_{FeO}.k.A}{W_{slag}}t$$

If f is the fraction reacted, then

$$f = \frac{(\%FeO)_o - (\%FeO)}{(\%FeO)_o}$$

Or,

$$1 - f = \frac{(\%FeO)}{(\%FeO)_o}$$

Consequently,

$$-\ln(1 - f) = \frac{100.M_{FeO}.k.A}{W_{slag}}t \quad (16)$$

A graph of $-\ln(1-f)$ versus t is linear with slope $\partial C/\partial t$ from which the rate constant can be calculated:

$$k = \frac{W_{slag}}{100.M_{FeO}.A} \left(\frac{\partial C}{\partial t} \right) \quad \text{mol cm}^{-2} \text{ s}^{-1} \quad (17)$$

Determination of the reaction area is difficult. However, for uniform internal reduction kinetics, the usable pore surface area of wustite per unit mass of wustite remains constant throughout the reaction (Fortini and Fruehan, 2005). The “intrinsic reaction rate constant per unit area of wustite” and the “usable surface area of wustite” could be combined together into one parameter, which is the product of the rate constant of the wustite reduction reaction per unit mass of wustite and the instantaneous mass of wustite in the system.

$$k' = \frac{W_{slag}}{100.M_{FeO}} \left(\frac{\partial C}{\partial t} \right) \quad \text{mol s}^{-1} \quad (18)$$

Where, k' , W_{slag} , M_{FeO} , $(\%FeO)_o$ and $(\%FeO)$ are the apparent rate constant, weight of slag, molar mass of FeO, initial concentration of FeO in the slag and concentration of FeO in the slag at time t , respectively.

1.6 Conversion Ratio (of CO and H₂ from waste plastics)

The amount of the hydrogen and carbon converted into utilisable gases from the waste plastic material during the reduction process was expressed in the form of a conversion ratio, similar to the definition by Ueki et al, 2008.

$$\% \chi_H = \frac{H_G}{H_{waste}} \times 100 \quad (19)$$

$$\% \chi_C = \frac{C_G}{C_{waste}} \times 100 \quad (20)$$

Where, % χ_H and % χ_C are the conversion ratios of hydrogen and carbon respectively. H_G (mol) and C_G (mol) are the amounts of hydrogen atom and carbon atoms in the recovered gases, respectively. H_{waste} (mol) and C_{waste} (mol) are the amounts of hydrogen atom and carbon atom, respectively, in the initial waste plastic materials.

2 Experimental

2.1 Sample Selection

EAF slag having an iron oxide composition of 47.1% Fe₂O₃ was obtained from OneSteel Sydney Mill, Rooty Hill NSW, Australia, which was further analysed by XRF and its composition is given in Table 1. Granulated 'pure water' plastic sachet bags (obtained from the Timber Market, Koforidua-Ghana) were employed in this study as reducing agent. The chemical composition (wt %) of the EAF slag and the elemental analysis of the plastic sachet bags are given in Tables 2 and 3, respectively.

Table 2 Chemical composition of EAF slag used in current study

Component	Composition (wt %)
CaO	24.1
Fe ₂ O ₃	47.1
Al ₂ O ₃	4.9
SiO ₂	9.6
MgO	10.2
MnO	4.8
Basicity B3 = %CaO/(%SiO ₂ +%Al ₂ O ₃)	1.66

Table 3 Elemental Analysis of plastic sachet bags (HDPE)*

Component	Wt %
Carbon	85.5
Hydrogen	14.2
Sulphur	0.3
Nitrogen	-
HHV (kJ/g)	46.5

(*- analysis conducted at Amdel laboratories, Newcastle, Australia)

2.2 Experimental Procedure

The EAF slag and plastic sachet bags were crushed in a jaw crusher and vibrating grinder to a particle size < 1.0 mm. Fixed masses of the slag (3.826 g) were subsequently mixed with the plastics in such a way as to maintain a fixed C/O ratio of about 2.0. The iron oxide –plastics blends were compacted in a specially designed die to produce cylindrical pellets (12 mm thick and 15 mm diameter), by applying a load of 7.5 tonnes for 2 minutes in a hydraulic press. Pellets were formed without binder addition as the plastic material provided the necessary bonding required for holding the particles of the pellet together. In this work, the plastics were mixed with the slag and reduction studies were performed without devolatilisation of the former, in order to fully ascertain the effect of the hydrogen from the plastics on the reduction process.

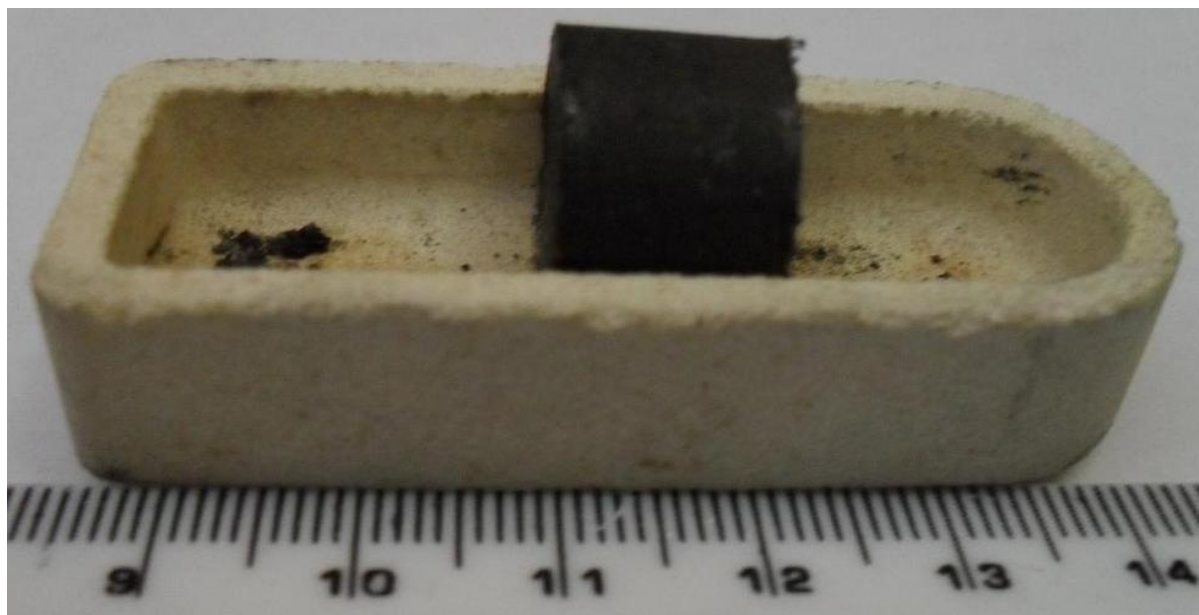


Fig. 2 Cylindrical pellet of EAF Slag + Waste Plastic Sachet Bags

A LECO crucible, having an XRF chemical composition as shown in Table 4 was selected as the sample container that was placed in a custom-made horizontal resistance heated furnace (Figs. 3 and 4), for the reduction studies. The volumes of CO and CO₂ evolving from the reaction assembly were measured continuously through an on-line infrared gas analyser. A gas chromatographic analyser (SRI 8610C Chromatograph Multiple Gas #3 GC configuration) equipped with a thermal conductivity detector (TCD) was also attached to this system to monitor CO, CO₂, H₂, H₂O and CH₄ gases produced by the reduction reaction and the results were recorded in a data-logging computer. The sample assembly was inserted in the furnace, which was purged continuously with a 1L/min argon of 99.99% purity to remove any contaminants and oxygen.

Table 4 Chemical composition (XRF) of LECO crucible used for this investigation

Component	Composition (wt %)
Al ₂ O ₃	3.73
SiO ₂	38.86
ZrO ₂	51.86
MoO ₃	1.77
HfO ₂	1.17
TiO ₂	0.36
Fe ₂ O ₃	0.10
RuO ₂	0.24
Rh ₂ O ₃	0.15
Others	1.76

After the furnace had attained the desired hot zone temperature (1550°C), the sample was pushed in the reaction hot zone and gases were monitored for 30 minutes. The time was selected since initial trials showed no significant changes in gas composition or degree of reduction beyond 30 minutes. A high resolution charge-coupled device (CCD) camera fitted with an IRIS lens was used to capture the live in-situ phenomena in the furnace.



Fig. 3 Pictorial representation of the horizontal furnace

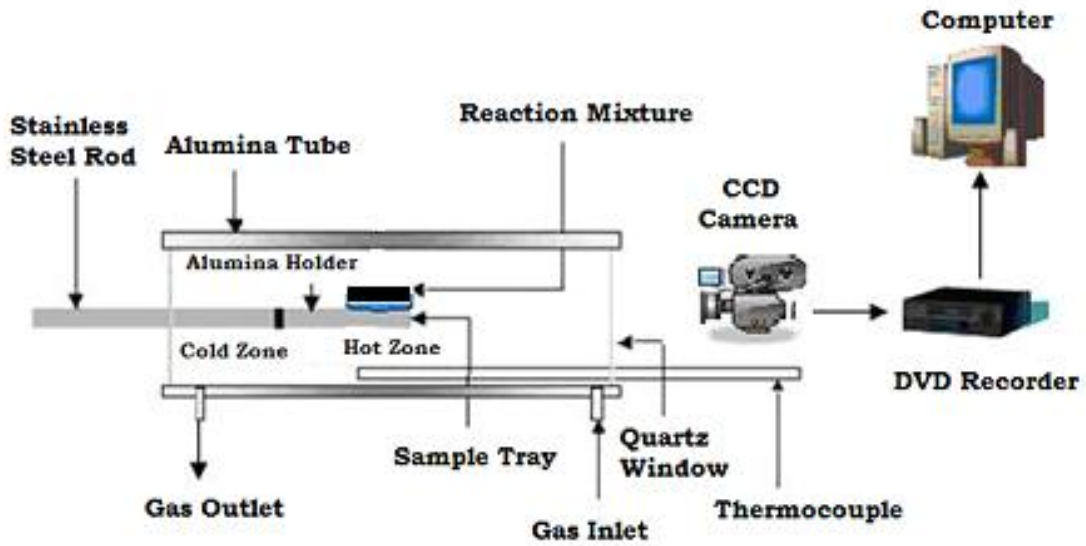


Fig. 4 Schematic representation of the horizontal furnace

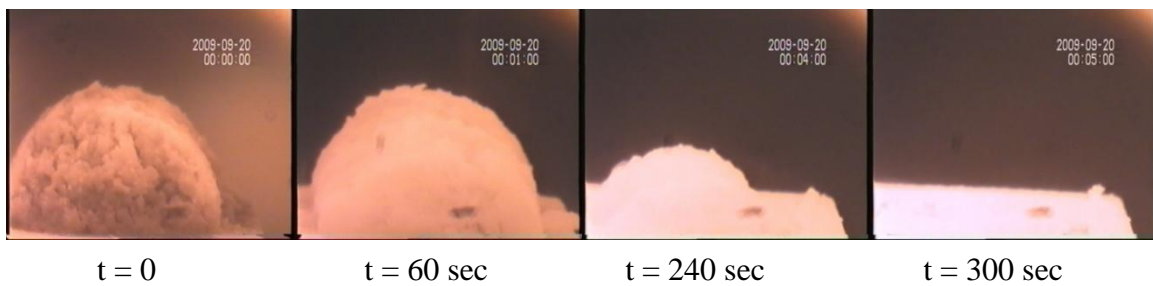
Reacted carbonaceous material/slag samples were quenched by rapidly withdrawing the tray from the hot reaction zone into the cold zone of the furnace. Particles of reduced iron metal, which were clearly visible to the naked eye, were removed magnetically and analysed.

2.3 Results and Discussions

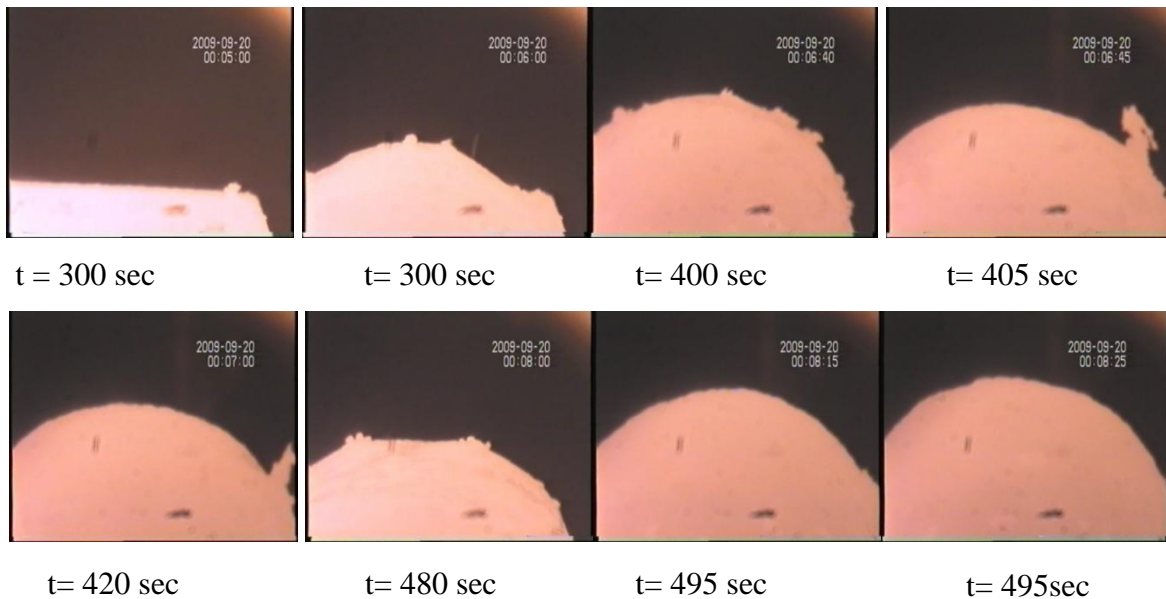
Stages of the reduction process

The sequence of processes that occurred, as captured by the CCD camera is shown in Fig. 5. Gas measurements began from the first minute and melting was complete after about 300 sec. The slag began to foam vigorously, immediately after the melting period and persisted for the next 210 sec before tapering off.

Stage 1: The melting process



Stage 2: Reduction and slag foaming



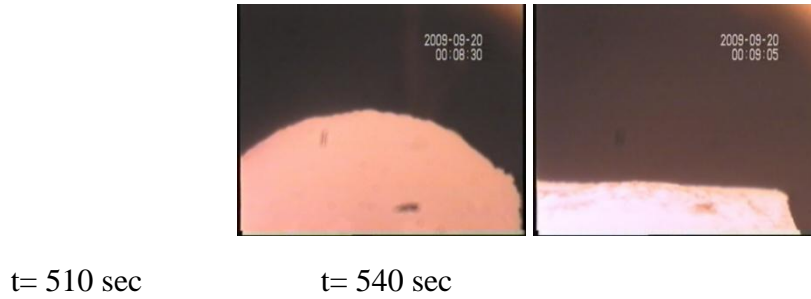


Fig. 5 Stages of the reduction process of FeO in slag by HDPE at 1550°C

Metal Production

Particles of reduced iron metal, which were clearly visible to the naked eye (Fig. 6), were removed magnetically and analysed chemically; the results indicated that about 83 percent reduction was achieved after 30 minutes of reduction.

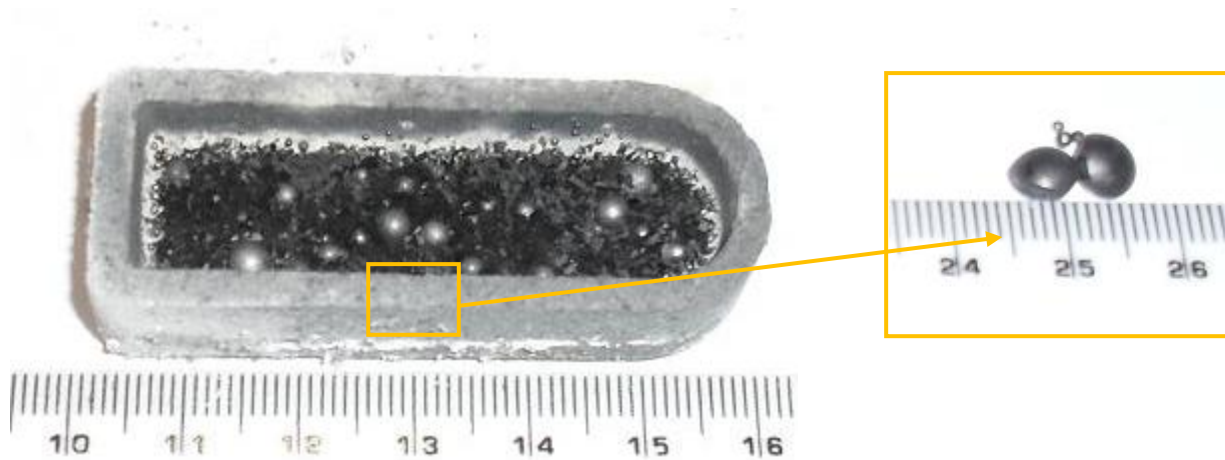


Fig. 6 Particles of metallic iron produced after reduction of EAF slag by 100% HDPE

Gas Emission Measurements by IR and GC

Gas generation rates for CO and CO₂ as measured by the infrared gas analyser are represented in figure 7. From this figure it is apparent that no significant amounts of CO or CO₂ was observed

in the first ten minutes of reduction, although over 60 percent of reduction was attained for all experimental runs within this period.

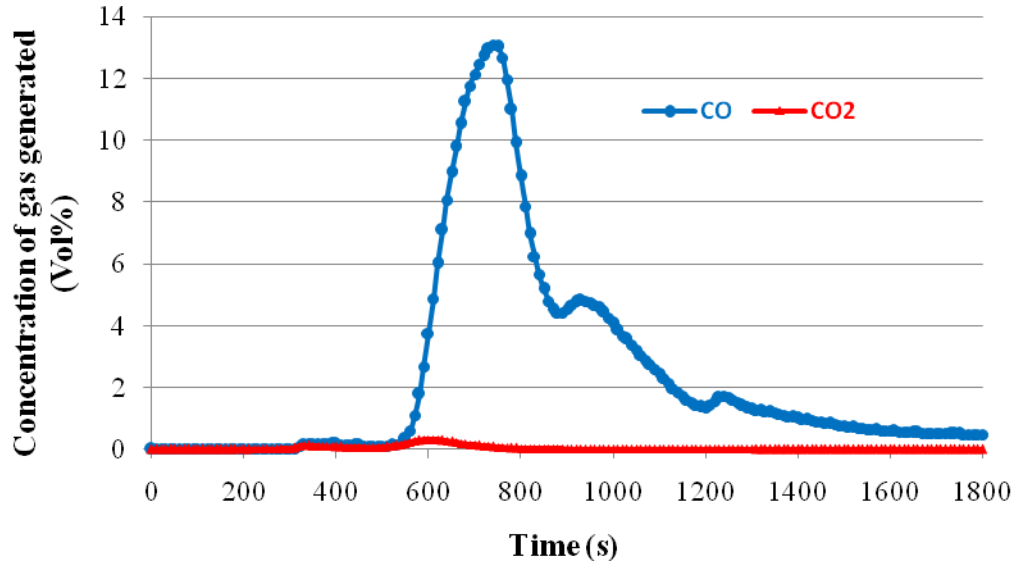


Fig. 7 Concentration of gases (CO and CO₂) generated from slag/HDPE composite pellet at 1550°C

Active gas generation commenced after about 9 minutes and rose rapidly from about 0.2 percent to about 13.0 percent in just three minutes. From the point of view that over 60 percent of metal reduction was achieved before either CO or CO₂ was evolved, active reduction of FeO could not have been effected by either solid C or gaseous CO since the product of such reduction should have been CO or CO₂ (even if rapid gasification of solid carbon by CO₂ or H₂O occurred). Accordingly, reduction of FeO could only have occurred with gaseous H₂ as reductant. The gas generation peaks as recorded by the GC are represented in figures 8 and 9 for the first ten minutes and after fifteen minutes respectively.

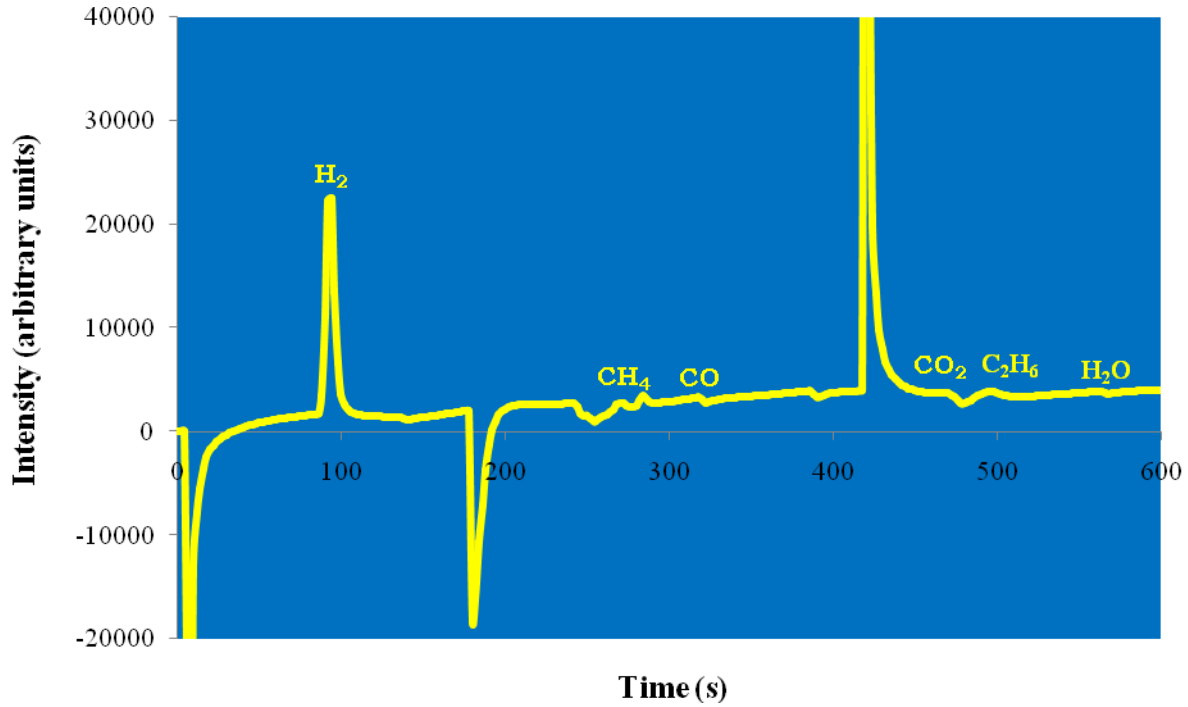


Fig. 8 Gas generation peaks (first 600 seconds) from slag/HDPE composite pellet at 1550°C

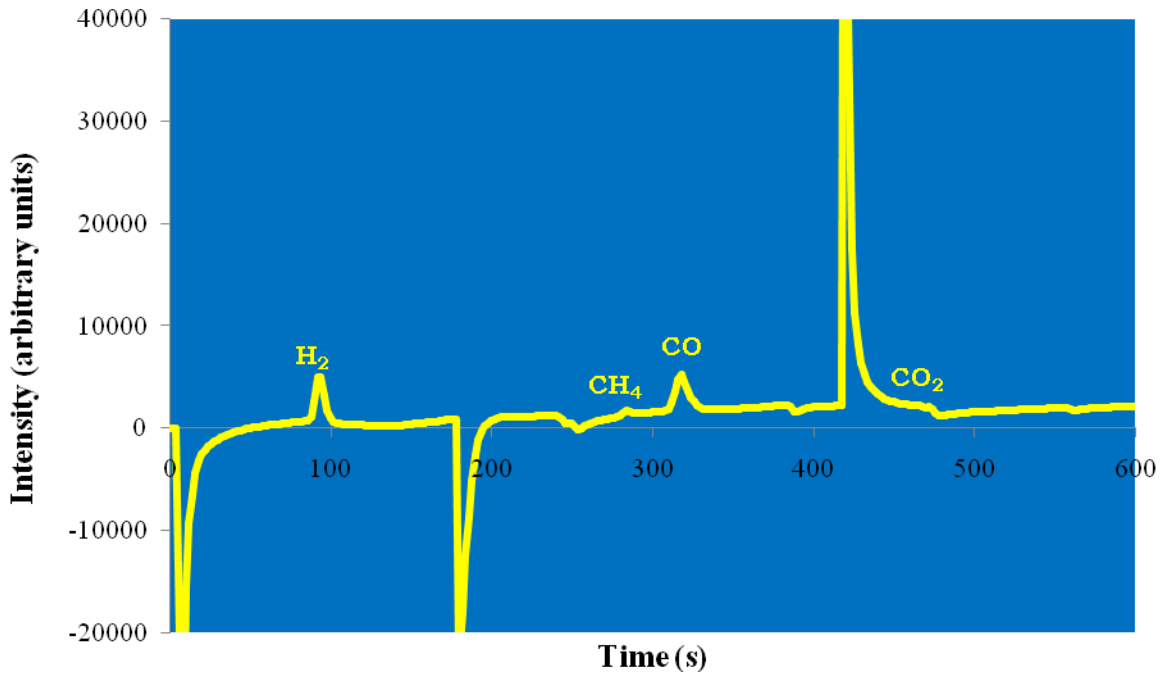


Fig. 9 Gas generation peaks (after 900 seconds) from slag/HDPE composite pellet at 1550°C

From figure 8, H₂ appears to be the major component of the gases detected as shown by the detection peaks. Minor peaks of H₂O were observed, probably due to the direct reduction of FeO by H₂. The quantity of H₂O was however low due probably to the reactions:



$$\Delta G^\circ = -33739.16 + 30.06T \text{ (J/mol)} \quad (\text{Kubaschewski et al, 1993})$$



$$\Delta G^\circ = 135,865.73 - 143.57 T \text{ (J/mol)} \quad (\text{Kubaschewski et al, 1993})$$

The direct reduction of iron oxides by CH₄ is also possible above 640 °C:



$$\Delta G^\circ = 241,985.6 - 261.73T \text{ [J/mol]} \quad (\text{Kubaschewski et al, 1993})$$

However, studies done by Hutchings et al (1988) in the temperature range 627 – 827°C indicate slow kinetics of reduction of the oxides by CH₄ unless metallic catalytic sites are formed for cracking of CH₄ (Sohn, 2005). It appears then that the reformation of CH₄ to CO and H₂ is more likely to occur according to any of the reactions below:



$$\Delta G^\circ = 191,940 - 223.24T \text{ [J/mol]} \quad (\text{Kubaschewski et al, 1993})$$



$$\Delta G^\circ = 488,580 - 539.36T \text{ [J/mol]} \quad (\text{Kubaschewski et al, 1993})$$

The reactions indicated by equations 22 and 23 are thermodynamically spontaneous above 590 °C and 633 °C respectively. From the gas measurement results of figures 7-10, reaction 23 appears to be more probable than reaction 22. It could be postulated that in the initial stages of

the reaction (up to about 9 minutes) when the composite is predominantly solid; H₂ reduces the oxides to form metallic (catalytic) reaction sites which assist in the cracking of CH₄ produced from the plastics. Overall, the fundamental reduction reaction occurs by reduction with CO and H₂ and with the overall elemental reducing gas as H₂ and CO, a reaction solely dominated by chemical kinetics can be described as a uniform internal reduction (Sohn, 2005).

The fact that H₂ is the predominant reductant in the first 10 minutes is confirmed by figure 10, which shows plots of percent reduction calculated from CO and CO₂ gas measurements and that from weight measurements. Clearly, FeO reduction by solid C or gaseous CO becomes important only after volatile reduction by H₂ has gone to completion.

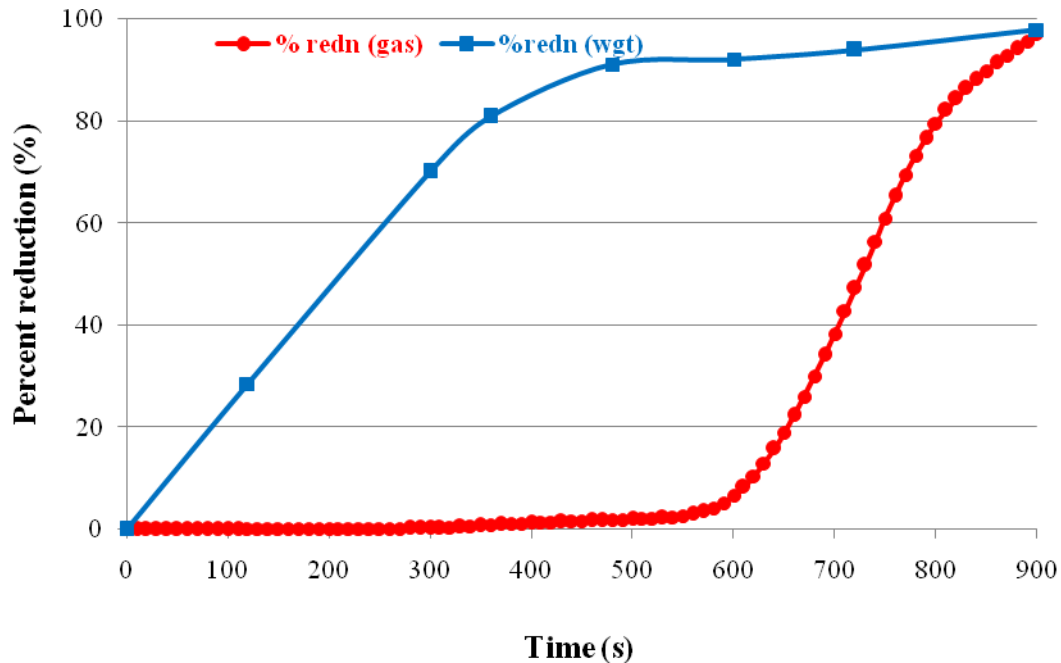


Fig. 10 Graph showing hydrogen gas as the predominant reductant in the first 600 seconds

Conversion Ratio (into CO and H₂ from waste plastics)

The composition of the active components of the off gas (measured by the GC3 analyser) along with the calculated conversion ratios for both atomic C to CO and atomic H to H₂ and the syngas content (%CO + %H₂) are presented in Table 5.

Table 5 Conversion ratio into H₂ and CO along with active components of the off gas

Expt. No. and time	%H ₂	%CO	%CO ₂	%CH ₄	%CO+%H ₂	% χ_H	% χ_C
1 @ t = 180 s	83.8	9.9	0	6.3	93.7	86.9	61.0
2 @ t = 480 s	82.6	11.9	0	5.5	94.5	89.0	68.2
3 @ t = 900 s	65.1	14.6	7.2	13.1	79.7	71.3	41.9
Average	77.2	12.1	2.4	8.3	89.3	82.4	57.0

Measured values of (%CO + %H₂) at 1550 °C ranged from about 80 percent to 95 percent with a mean a value of about 89 percent. Even though the experimental conditions are different and reduction studies were conducted on iron oxide from slag (which is much more difficult than reduction of pure iron oxide) the results agree with those obtained by Matsuda et al., 2008 who reported a value of about 92% for the reduction of reagent grade Fe₂O₃ with polyethylene in the temperature range 1400°C – 1800°C. The conversion ratio into H₂ was in the range 71-89% while that into CO ranged from about 42 to 68%. Values obtained by Ueki et al., 2008 for the reduction of reagent grade Fe₂O₃ by polyethylene were in the range of 60-70% and 70-80% for conversion into H₂ and CO, respectively, at 1300°C.

Percent reduction by carbon/carbon monoxide

The graph of percent reduction against time is linear when the composite pellet was in the solid state. The graph for the molten state reduction process was fairly linear between 600 and 750 s, beyond which linearity of the graph disappears. The nonlinear region may be described by a degradation period characterised by local deficiency of FeO at the gas/slag interface (Min et al, 1999).

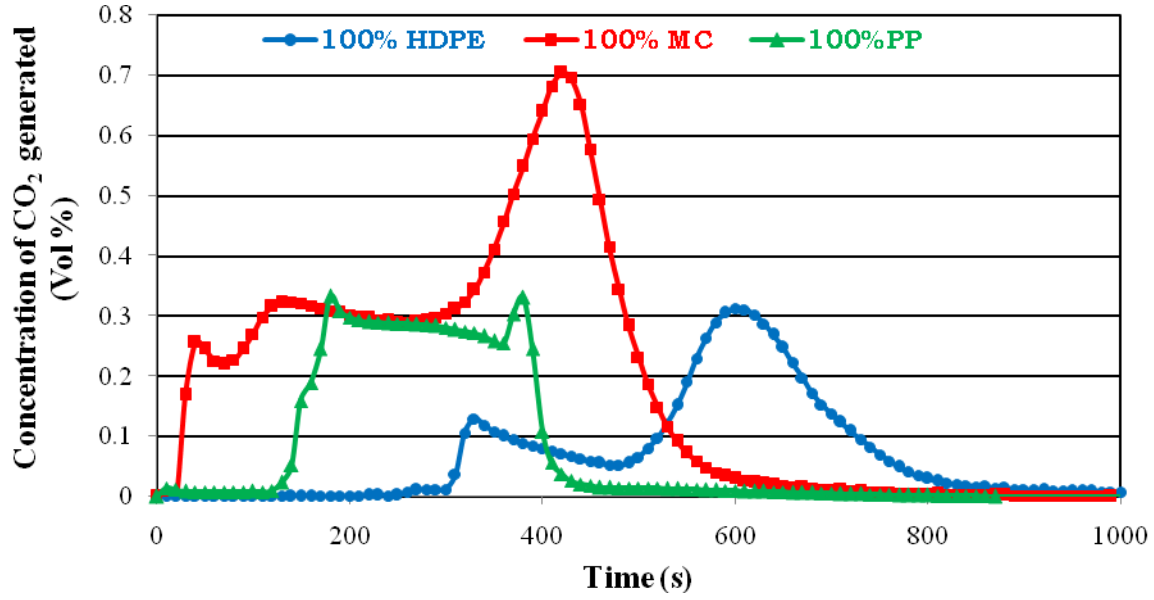


Fig. 11 Comparison of CO₂ emissions from HDPE those of polypropylene (PP) and conventional metallurgical coke as a reductants at 1550°C

In the solid state, before commencement of melting

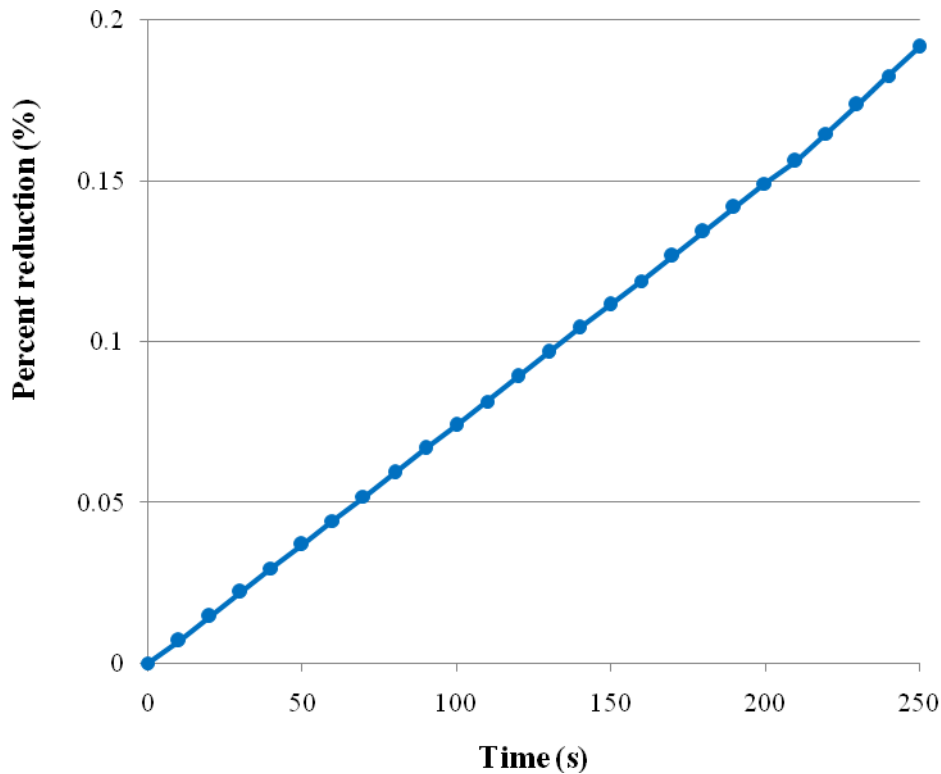


Fig. 12 Percent reduction for the first 250 s (before melting)

Reaction kinetics

Graphs of $-\ln(1-f)$ were plotted against t for the solid and molten state regions and are represented in figures 13 and 14 respectively.

In the molten state

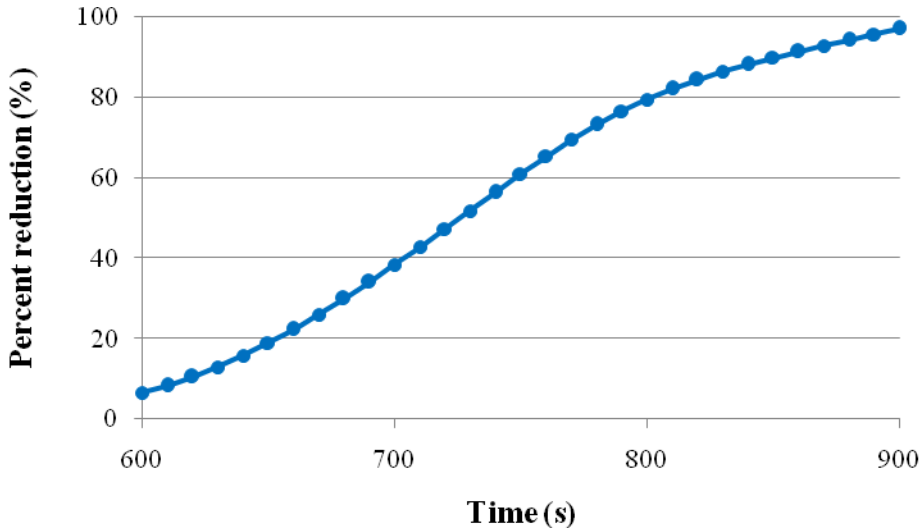


Fig. 13 Percent reduction during melt

Solid state kinetics

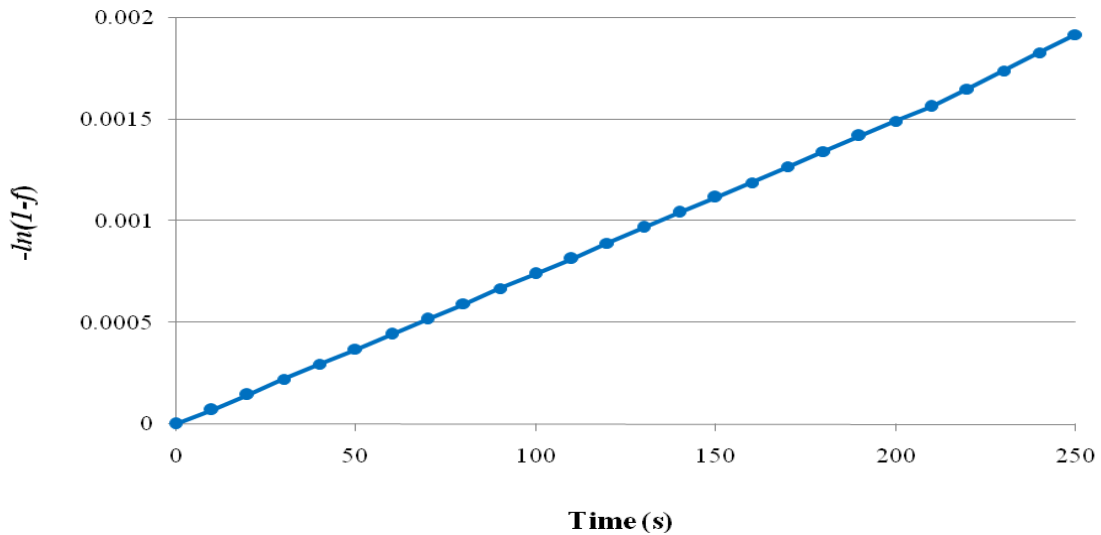


Fig. 14 Plot of $-\ln(1-f)$ vs. time for the solid state reduction slag/plastics composite pellet at 1550°C

The linear section observed in the solid state region is an indication of chemical control process. In the molten state, the graph has a fairly linear region, indicating a mixed kinetics by both chemical control and mass transfer. Without the contribution by H_2 to the reduction process, the apparent rate constants are $4.08 \times 10^{-7} \text{ mol s}^{-1}$ and $7.21 \times 10^{-6} \text{ mol s}^{-1}$ for the solid state and molten state reduction process, respectively. When the contribution of hydrogen is taken into consideration the only linear section of the graph, which lies predominantly in the solid region has an apparent rate constant of $1.23 \times 10^{-4} \text{ mol s}^{-1}$. The huge discrepancies in these values suggest that the contribution by C or CO in the initial stages of the reaction (where H_2 is in large excess) is negligible. This is not surprising since H_2 is a faster reductant than CO and solid carbon.

CO₂ Emissions to the Environment

The CO₂ content in the off gas as measured continuously during the reduction of the FeO in slag with HDPE as reductant is compared to those from PP and conventional metallurgical coke under the same experimental conditions and the results are presented in figure 11.

Molten state kinetics

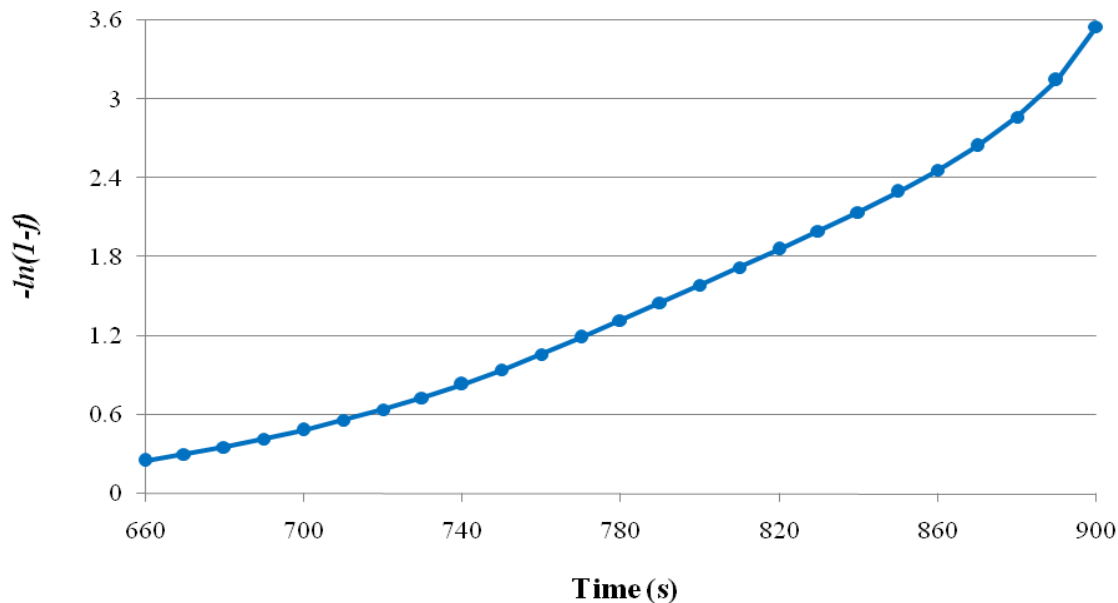
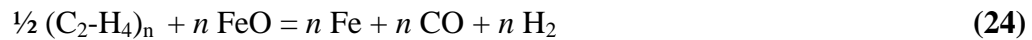


Fig. 15 Plot of $-\ln(1-f)$ vs. time for the molten state reduction slag/plastics composite pellet at 1550°C

The superiority of the polymers (HDPE and PP) over conventional metallurgical coke as environmentally benign reductants is apparent from figure 11. While there is no clear distinction between the two polymers with respect to the level of CO₂ evolved, it is clear from the figure that CO₂ emission is delayed for HDPE, attaining its maximum after about 10 minutes of reduction. Within this period, a greater reduction of the FeO would have been achieved; in fact in a significant number of the experimental runs, over 90 percent reduction was achieved before ten minutes, when HDPE was used as a reductant. Theoretically it is possible to produce metallic iron and synthesis gas (CO + H₂) from iron oxide/polymer composites as illustrated in equation 24.



This investigation has shown that it is possible to drastically reduce CO₂ emissions by using waste polymeric materials like pure water sachets (HDPE) as reductants in the carbon composite method. Further research is currently ongoing to establish the optimum conditions needed for maximum productivity and 'zero tolerance' for CO₂ emissions.

3 Conclusions

Feasibility studies on the production of metallic iron and syngas from EAF slags using waste plastics sachet bags as reducing agent using the iron ore/carbon composite method have been conducted. Major findings of this investigation are:

1. Pure water 'sachet', which is manufactured from high density polyethylene, can be used effectively as a reductant in iron and steel making technologies.
2. Synthesis gas (CO + H₂) that constitute up to about 95% of the total gas volume generated through the gasification and reduction process can be recovered as a useful by-product.
3. The potential to reduce carbon dioxide emissions exists, especially if waste plastics are used as reductants in the iron ore/carbon composite method.

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