

## Effect of Waste Plastics (HDPE) Addition on the Reduction, Carburisation and Desulphurisation of Iron Oxide by Petroleum Coke

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### Abstract

Large amounts of petroleum coke are produced during the industrial processing of crude oil. Petroleum coke is unsuitable as a reductant in iron and steel technologies owing to the high sulphur content. In this work the effect of blending petroleum coke with high density polyethylene (HDPE) on the reduction of iron oxide and the carburisation and desulphurisation of the reduced metal was investigated in a horizontal tube furnace. Composite pellets of blends of petroleum coke and HDPE with EAF slag (47.1 wt. % FeO) were heated rapidly in a horizontal tube furnace at 1550 °C in a stream of argon. Reaction products were analysed using an IR gas analyser and a gas chromatography unit. The reduced metal was analysed for its carbon and sulphur contents using a LECO<sup>TM</sup> Carbon/Sulphur and LECO<sup>TM</sup> Oxygen/Nitrogen analysers, respectively. The results indicate that petroleum coke-HDPE blends can be utilised successfully as reductants for iron oxide reduction; significant improvements in the extent of reduction (after fifteen minutes), carburisation and desulphurisation of the reduced metal were observed when petroleum coke was blended with HDPE.

### 1. Introduction

Large amounts of petroleum coke are produced during the industrial processing of crude oil. Petroleum coke is unsuitable as a reductant in iron and steel technologies owing to its high sulphur content. To be useful as a reductant, petroleum coke is often subjected to pre-treatment processes like thermal calcination and hydrogenation to decrease the sulphur content. Several methods of desulphurising petroleum coke have been proposed [1-9] with none touching on the removal of sulphur by blending of coke with waste plastics. Besides, these pre-treatment steps present additional

cost factors, especially if done separately from the iron oxide reduction step. Previous research [10] on the reduction of FeO from EAF slag demonstrated that blending of metallurgical coke with HDPE has a significant attenuating effect on the content of sulphur in the reduced metal. Similar results were obtained when metallurgical coke was blended with end-of-life rubber tyre containing high levels of sulphur [11]. Accordingly, in this work the effect of HDPE blending on the reduction of FeO from EAF slag is discussed along with its effect on the content of sulphur in the reduced metal.

## 2. Experimental

### 2.1 Sample selection

Petroleum coke, HDPE and blends of petroleum coke with HDPE (Blends 1-4) (Fig. 1) were employed in this study as reductants. The chemical composition of the carbonaceous samples is given in Table 1. An EAF slag (47.1% FeO) having basicity (B3) of 1.66 (obtained from OneSteel Sydney Mill, Australia) was utilised as the source of iron oxide; its XRF composition is given in Table 2.

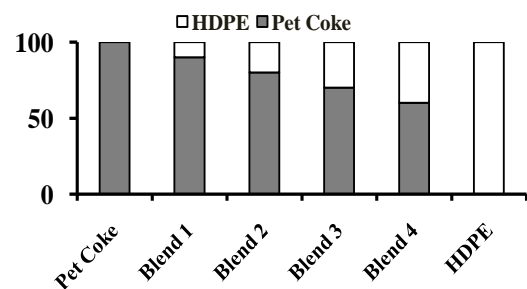


Fig. 1: Blend compositions of the carbonaceous materials used

Table 1: Chemical composition of petroleum coke and HDPE

Component	Pet Coke (wt %)	HDPE (wt %)
Moisture	0.04	-
Volatile Matter	0.21	99.70
Ash	0.10	0.30
Total Carbon	99.86	85.5
Fixed Carbon	99.65	-
Hydrogen	-	14.2
Sulphur	2.81	0.30

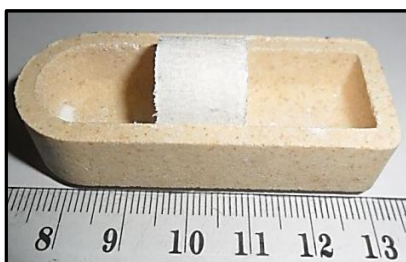
Table 2: Composition of EAF slag used

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

## 2.2 Sample preparation

### 2.2.1 Thermal decomposition studies

Pulverised HDPE sample (particle size below 1 mm) was mixed thoroughly with alumina powder and cylindrical pellets were formed from the resulting mixture by applying a load of 7.5 tonnes for 1 minute in a hydraulic press. The use of the alumina powder was to slow down the decomposition process (to enable gas measurements by the IR-analyser) as well as mimic the reduction environment through the cylindrical pellets. The alumina powder acted as a blank medium, since its reduction will be difficult at the selected temperature.

Fig. 2: Composite pellet (of Al<sub>2</sub>O<sub>3</sub> + HDPE) utilized for thermal decomposition of HDPE at 1550 °C

### 2.2.2 Reduction studies

The slag-carbonaceous blends were compacted in a specially designed die to produce cylindrical pellets (11.6-12.0 mm thick and 14 mm diameter) (Fig. 3), by applying a load of 7.5 tonnes for 1 minute in a hydraulic press. Petroleum coke-HDPE possessed self-binding properties and, accordingly, did not require the addition of any binder.

The mass of the composite pellet was fixed (~4.77 g) and it was comprised of ~ 3.83 g slag and ~ 0.94 g carbonaceous blend so as to have a C/O molar ratio ranging from 2.66 to 3.10. This ensures that excess carbon is available in the system to allow for the reactions to reach completion as well as restrict the content of H<sub>2</sub>O in the off-gas to negligible levels. In this ratio the 'O' refers to the oxygen content of the FeO in the slag while the 'C' refers to the total carbon from petroleum coke and HDPE in the blend.

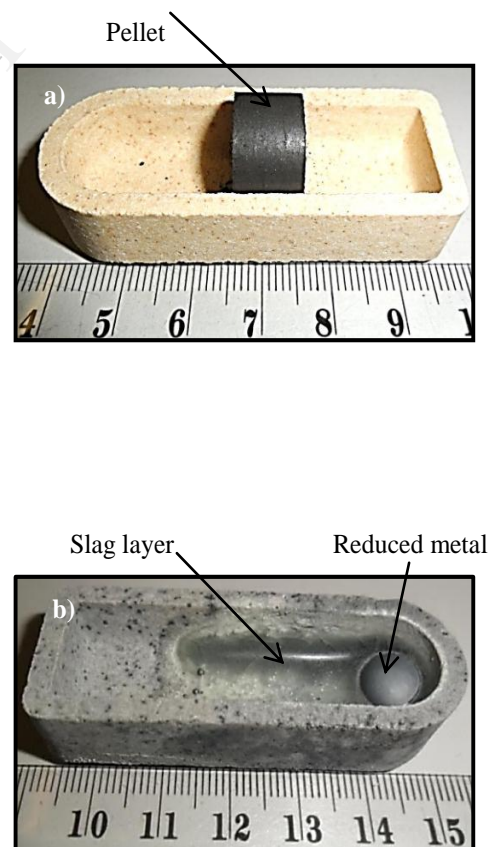


Fig. 3: Composite pellet (slag + HDPE): a) before reduction and b) after reduction at 1550 °C

## 2.3 Experimental procedure

### 2.3.1 Thermal decomposition experiments

The experimental apparatus consisted of two gas analysers connected to an electrically heated horizontal tube furnace and a data logging computer (Fig. 3). CO, CO<sub>2</sub> and CH<sub>4</sub> were monitored continuously by an IR gas analyser (Advance Optima model ABB® AO2020) while a GC analyser (SRI 8610C Multiple Gas Chromatograph #3 configuration, equipped with a thermal conductivity detector, TCD) monitored O<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O and C<sub>n</sub>H<sub>m</sub>.

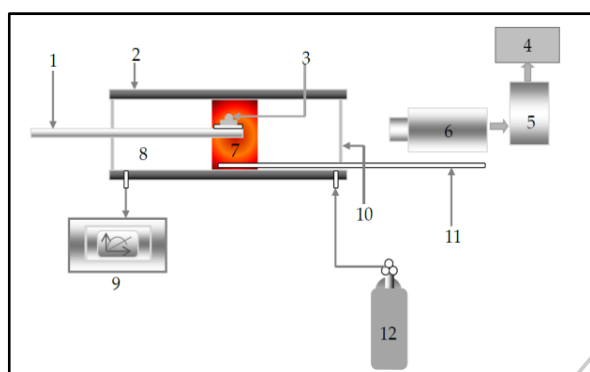


Fig. 4: Schematic of the horizontal tube furnace and IR gas analyser system. (1 Sample Rod; 2 Alumina tube; 3 Reaction mixture; 4 PC; 5 DVD; 6 CCD Camera; 7 Hot Zone; 8 Cold Zone; 9 Gas analyser; 10 Quartz window; 11 Thermocouple; 12 Argon gas)

The furnace was purged continuously with argon gas (99.995% purity) to ensure an inert atmosphere. The furnace was preheated to the desired temperature and the sample was inserted; gas measurement commenced immediately after insertion and continued for 20 minutes. No appreciable change in gas composition was observed beyond 20 minutes.

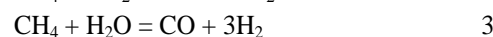
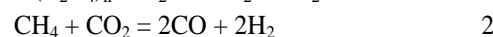
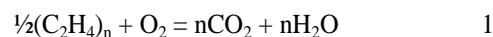
### 2.3.2 Reduction experiments

The reduction experiments were conducted in a similar way as the thermal decomposition process, except that composite pellets in this case contained slag instead of alumina. After the furnace had attained the desired hot zone temperature, the sample was pushed into the reaction hot zone and gases were monitored for 15 minutes.

## 3. Results and discussions

### 3.1 Thermal decomposition behaviour of HDPE at 1550 °C

The gas generation behaviour during the thermal decomposition of HDPE-alumina at 1550 °C is illustrated in Fig. 5. The predominant gases from the thermal decomposition of HDPE are the reducing gases CH<sub>4</sub> and H<sub>2</sub> (peak identified in Fig. 6). Minor amounts of CO and CO<sub>2</sub> were detected as indicated in Fig. 4. As alumina was unlikely to have been reduced by HDPE (and the HDPE had no oxygen), the only probable source of CO and CO<sub>2</sub> could be from partial oxidation of the HDPE by trapped oxygen in the pores of the HDPE-alumina compact and/or minor reformation of CH<sub>4</sub> by H<sub>2</sub>O and/or CO<sub>2</sub> (equations 1-3).



However, the contents of CO and CO<sub>2</sub> were negligible compared to H<sub>2</sub> and CH<sub>4</sub> when HDPE-alumina was heated at 1550 °C.

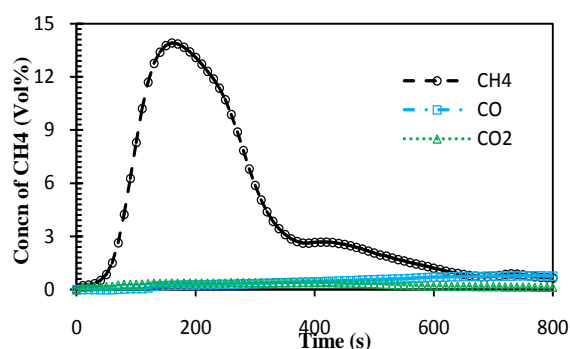


Fig. 5: Gas generation behaviour during the thermal decomposition of HDPE from a HDPE-alumina compact

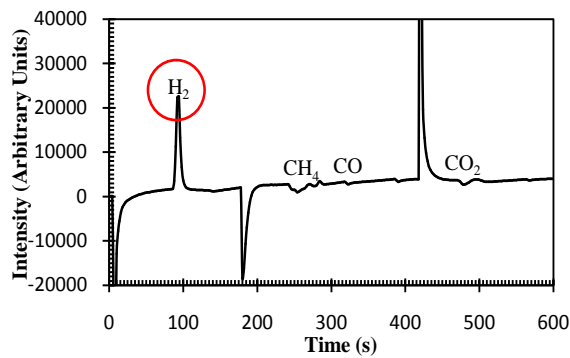
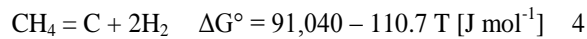


Fig. 6: Gas chromatogram obtained after 60 s of heating HDPE-alumina compact

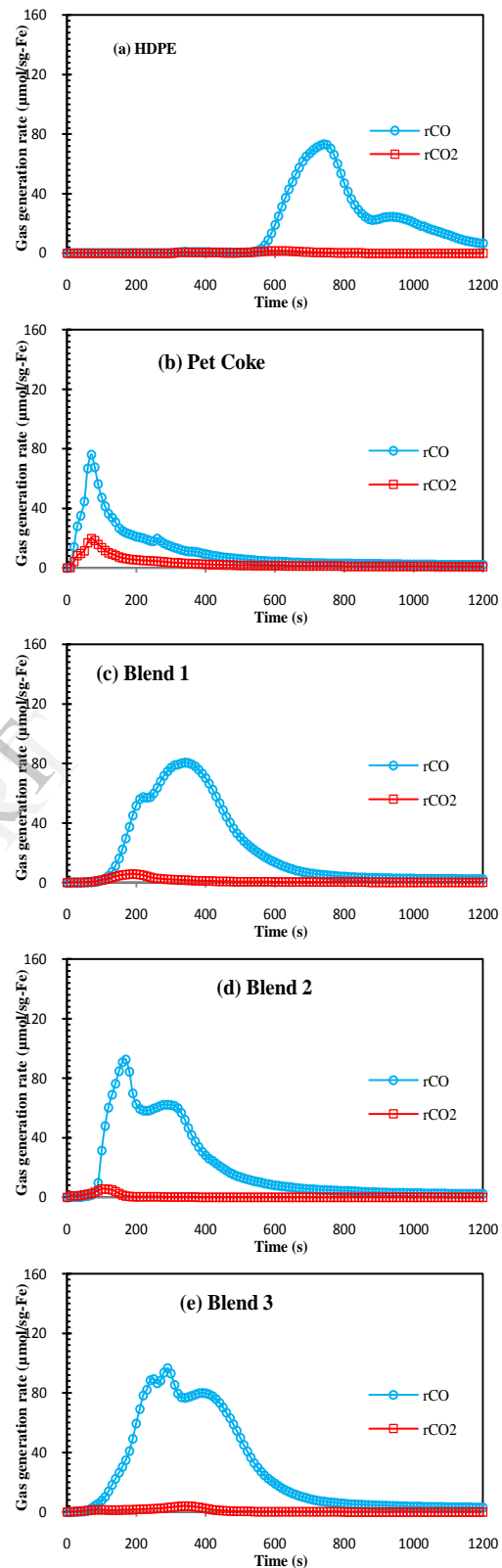
Direct ingress of oxygen into the furnace was unlikely as the furnace was purged continuously with argon. After 60 s of heating the compact, the area ratio  $H_2/CH_4$  was approximately 1.0 but this gradually increased to about 2.5 after 300 s, implying that  $CH_4$  undergoes cracking to generate more  $H_2$  and nascent C in the course of heating, probably through equation 4, which is spontaneous above 550 °C.



It is clear from Figs 5 and 6 that the main reductants produced from the thermal decomposition of HDPE are  $H_2$ ,  $CH_4$ , and minor amounts of CO and C. The generated carbon particles are present at the Nano-scale level. The potential for HDPE to function as a reductant for iron oxide reduction therefore exists, as indicated by the formation of Nano-scale solid carbon and gaseous  $H_2$  and  $CH_4$ .

### 3.4 Gas generation rates (IR analyser)

The contents of CO and  $CO_2$  in the off-gas were measured continuously by an infrared (IR) gas analyser from which the rates of gas evolution ( $\mu\text{mol/s.g-Fe}$ ) were calculated for each carbonaceous blend. The results are shown in Fig. 7.



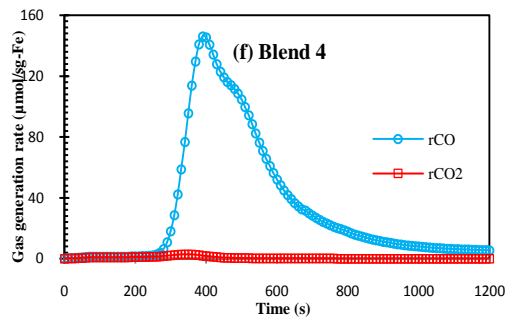


Fig. 7:Rate of gas generation as a function of time during the reduction of FeO in slag by each reductant at 1550 °C

The rate of evolution of CO increased slowly for the first 400 seconds for coke followed by a sharp rise, attaining a maximum value after about 570 seconds. The rate of CO generation for HDPE became significant after about 550 seconds, attaining its maximum value after about 740 seconds. The maximum rate of CO increased with the amount of HDPE blended with Pet Coke.

### 3.5 Extent of reduction

The reduced metal was weighed and the content of oxygen was determined using a LECO Nitrogen/Oxygen analyser (model TC-436 DR 602-500-600, LECO Corporation, Michigan, USA). The extent of reduction after 900 s was determined from the calculated oxygen values with the knowledge that the initial concentration of removable oxygen from the reducible component of the slag (FeO) is about 22.27%. The results are shown in Table 3 which indicates that blending of pet coke with HDPE resulted in a progressive increase in the extent of reduction. The reasons for the observed improvement in extent of reduction with HDPE addition are explained elsewhere [10, 11].

Table 3: Extent of reduction achieved by each reductant after 900 s

Reductant	Extent of reduction (%)
Pet Coke	85.3
Blend 1	98.4
Blend 2	97.9
Blend 3	90.1
Blend 4	95.7
HDPE	85.6

### 3.6 Nature of reduced metal

Complete separation of the metal from slag is an important requirement for decreasing the levels of impurities in the reduced metal. Fig. 8 shows the nature of the metal produced from reduction of the slag by pet coke and Blend 1 at 1550 °C.



Fig. 8: Nature of metal produced from reduction of slag by (a) Pet coke and (b) Blend 1

### 3.7 Carburisation and desulphurisation of the reduced metal

Carburisation of the reduced metal is required for lowering its melting temperature and obtaining a melt and slag separation at molten state. The contents of carbon and sulphur in the reduced metal were determined using a LECO Carbon/Sulphur analyser (model CS 230, LECO Corporation, Michigan, USA); the results are shown in Figs. 9 and 10 for carbon and sulphur respectively. Carburisation is lowest for HDPE (0.0093 wt %), followed by petroleum coke (1.5155 wt %). It increases consistently with the amount of HDPE blended with petroleum coke up to Blend 4 (3.83 wt %). The carburisation process for each of the blends is higher than either petroleum coke or HDPE alone, indicating the existence of a favourable synergetic



effect between petroleum coke and HDPE towards carburisation of metallic iron.

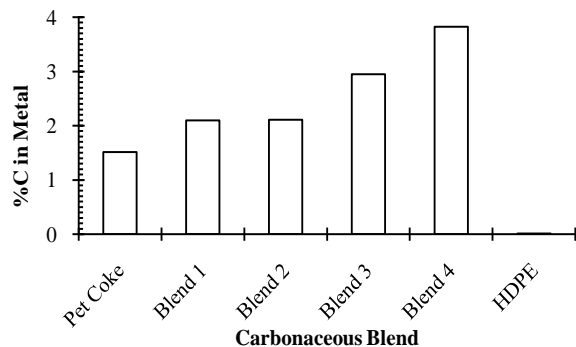


Fig. 9: Carburisation of reduced metal by various reductants at 1550 °C

As was observed in previous investigations the reduced metal was spherical in each case, indicating that it was formed from the liquid state. Although the experimental temperature of 1550 °C is only slightly above the melting point of iron (1536 °C), the levels of carburisation observed in this investigation for the blends are sufficient for the metal produced to undergo melting. For raw HDPE, as was mentioned in a previous investigation for coke-HDPE blends [10], it is believed that metal was highly carburised initially but the reactive carburised metal participated in the reduction of other oxides in the slag as was demonstrated by Dankwah [12] for coke-HDPE blends. The level of sulphur in the metal (Fig. 10) showed a reverse trend to that seen for the carbon pickup, with the highest level of sulphur (0.187 wt %) found in the metal produced using pet coke. Blending of pet coke with HDPE resulted in a consistent decrease in the level of sulphur in the reduced metal, with no sulphur detected in the metal produced using Blend 4 as reductant.

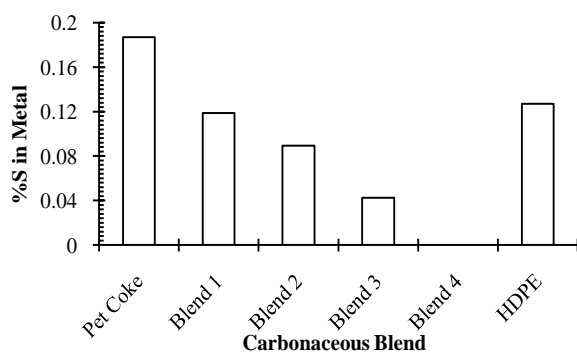
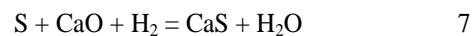
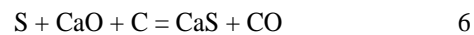


Fig. 10: Content of sulphur in reduced metal after reduction of FeO in slag by various pet coke-HDPE reductants at 1550 °C

Sulphur removable from the reduced metal may occur through a hydrodesulphurisation process represented by equation 5 or through a direct removal by CaO into the slag phase (equation 6 and or 7):



In this investigation the contribution of equation 5 to the overall desulphurisation process was not significant because when Fe<sub>2</sub>O<sub>3</sub> (with virtually no CaO or MgO) replaced the slag as the source of iron oxide, no significant difference was observed in the levels of desulphurisation among the reductants. Accordingly, CaO played a major role in sulphur removal, with equation 6 being the predominant reaction when petroleum coke was used as the reductant. When petroleum coke was blended with HDPE both equation 6 and equation 7 contributed to the desulphurisation process. Besides, as was explained in previous investigations [10-12], a decrease in the time required for complete melting of the slag was observed with an increase in the content of the polymer. This improvement in apparent fluidity of the slag could promote the diffusion of calcium sulphide to the slag layer and in the process promote the removal of sulphur from the reduced metal.

#### 4. Conclusions

The effect of HDPE addition on the reduction of FeO in EAF steelmaking slag by pet coke has been investigated by experiments conducted in a laboratory-scale horizontal tube furnace; the major findings of the investigation are:

- (1) Blends of pet coke with HDPE could be used effectively to reduce FeO from EAF slag.
- (2) Significant improvements in the extent of reduction were observed when pet coke was partly blended with HDPE.

(3) The degree of carburisation of the reduced metal improved considerably when pet coke was blended with HDPE. It improved from 1.52 wt % (pet coke) to 3.83 wt % (Blend 4) and then decreased to 0.0093 wt % (HDPE).

(4) The content of sulphur in the reduced metal was slightly lower in HDPE (0.127 wt %) compared to that of pet coke (0.187 wt %). However, blending resulted in a drastic decrease in sulphur for all the blends, with the reduced metal showing no sulphur when Blend 4 was used as reductant.

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