

Effect Of LLDPE Addition On The Reduction Of Feo From EAF Slags

James Ransford Dankwah, Emmanuel Baawuah

Abstract: The effect of waste linear low density propylene (LLDPE) addition on the reduction of FeO-containing slag by metallurgical coke has been investigated through experiments conducted in a laboratory scale horizontal tube furnace. Composite pellets of EAF slag (47.1% FeO) with coke, LLDPE and blends of coke/LLDPE (in four different proportions) were rapidly heated at 1520 °C under high purity argon gas and the off gas was continuously analysed for CO and CO₂ using an online infrared gas analyser (IR). The extent of reduction after ten minutes, level of carburisation and desulphurization were determined for each carbonaceous reductant. The results show significant improvements in extent of reduction along with improved levels of carburisation and desulphurisation of the reduced metal when coke was blended with LLDPE.

Index Terms: Linear low density polyethylene, Metallurgical coke; FeO reduction; Composite pellets, Infrared gas analyser, LECO carbon/sulphur analyser, LECO oxygen/nitrogen analyser, Extent of reduction, Carburisation; Desulphurisation.

1 INTRODUCTION

31.9% of (L)LDPE was recycled in Australia in 2011-2012 [1]. The rest was either landfilled or dumped illegally. This category of waste stream occupies large landfill space and is not biodegradable. LLDPE contains carbon and hydrogen and its thermal decomposition at high temperatures generates large amounts of the gaseous reducing species H₂ and CH₄ [2-5], which are known reductants of metal oxides. The use of waste polymeric materials as chemical feedstock in iron and steelmaking is currently gaining the attention of researchers [2-8]. LLDPE is a thermoplastic polymer having high levels of carbon and hydrogen, similar to HDPE. However, not much is known about the use of LLDPE as a reductant or carburiser in iron and steelmaking technologies. Accordingly, in this work, the potential feasibility of LLDPE and its blends with coke to function as reductant and carburiser is investigated through the composite-pellet-in-crucible approach. The main aims of this investigation are to investigate the potential feasibility of utilising LLDPE as reductant for iron oxide reduction and to determine the effect of LLDPE addition on the:

- extent of reduction of FeO in EAF slag by coke
- degree of carburisation and
- degree of desulphurisation of the reduced metal

2 EXPERIMENTAL

2.1 Raw Materials

Metallurgical coke and its blends in different proportions with granulated LLDPE (Fig. 1) were employed in this study as the carbonaceous materials. The chemical composition (wt %) of the carbonaceous samples (coke and LLDPE) and the ash analysis are given in Tables 1-3, respectively.

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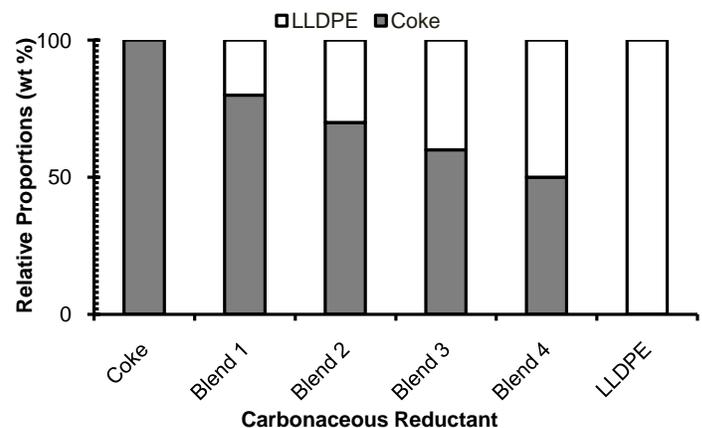


Fig. 1: Blend compositions of the different carbonaceous materials utilised in this study

Samples of CNS were ground and sieved to particle size in the range of -470 +450 μm while samples of granulated HDPE were crushed to smaller sizes by using a cutting mill "Pulverisette 15" (Fritsch GmbH, Idar-Oberstein, Germany). By means of a sieve insert with 0.5 mm trapezoidal perforations in the cutting mill a particle size -470 +450 μm, similar to that of CNS was obtained. Blends of CNS/HDPE were prepared in three different proportions.

TABLE 1: ELEMENTAL ANALYSES OF LLDPE AND COKE

Component	C	H	S
LLDPE (wt %)	85.5	14.3	0.2
Coke (wt %)	78.7	1.11	0.32

TABLE 2: PROXIMATE ANALYSES OF LLDPE AND COKE

Component	Moisture	Ash*	Volatile matter*	Fixed carbon*
LLDPE (wt %)	-	0.3	99.7	-
Coke (wt %)	4.60	18.30	3.0	71.70

*Dry basis

TABLE 3: ASH ANALYSIS OF COKE*

Component	Raw (wt %)
SiO ₂	50.7
Fe ₂ O ₃	4.8
Al ₂ O ₃	36.0
TiO ₂	1.4
P ₂ O ₅	1.6
CaO	3.3
MgO	0.94
Na ₂ O	0.39
K ₂ O	0.53
SO ₃	0.39

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

An EAF slag with 47.1 % FeO and basicity (B3) of 1.66 was provided by OneSteel Sydney Steel mill, which was further analysed by XRF and its composition is given in **Table 4**.

TABLE 4: COMPOSITION OF EAF SLAG USED FOR THIS INVESTIGATION*

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

2.2 Sample preparation

Samples of metallurgical coke were ground and sieved to particle size in the range of -470 +450 μm while samples of granulated LLDPE were crushed to smaller sizes by using a cutting mill "Pulverisette 15" (Fritsch GmbH, Idar-Oberstein, Germany). By means of a sieve insert with 0.5 mm trapezoidal perforations in the cutting mill a particle size -470 +450 μm, similar to that of metallurgical coke was obtained. The slag was subsequently mixed with the carbonaceous blends and compacted in a die to produce cylindrical pellets (11.6-12.0 mm thick and 14 mm diameter) (**Fig. 3a**), by applying a load of 7.5 tonnes for 1 minute in a hydraulic press.



Fig. 3: Cylindrical pellet (slag + carbonaceous material) placed in the LECO crucible prior to the experiments (b) spherical particle of reduced metal after reaction

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 2.44 to 2.66. This ensures that excess carbon is available in the system to allow for the reactions to reach completion. In this ratio 'O' refers to the oxygen content of FeO in the slag while 'C' refers to the total carbon from coke and LLDPE in the blend. The carbonaceous blend composition chart is shown in **Fig. 1**. Preliminary trials showed that crucibles (supplied by LECO Australia) were the most suitable for the current investigations since they were not attacked extensively by the molten slag as was observed when aluminosilicate crucibles were used. The LECO crucibles were primarily composed of zirconia (~51 wt %), silica (~39 %) and alumina (~3.7%)

2.3 Experimental procedure

The experimental procedure involved three parts: the reactions in a custom-made horizontal resistance heated furnace (**Fig. 3**), visual observation using a CCD camera and off-gas analysis using a gas chromatographic analyser (SRI 8610C Chromatograph Multiple Gas #3 GC configuration equipped with a thermal conductivity conductor (TCD)) and a continuous infrared gas analyser, to monitor off-gases produced by the reduction reaction.

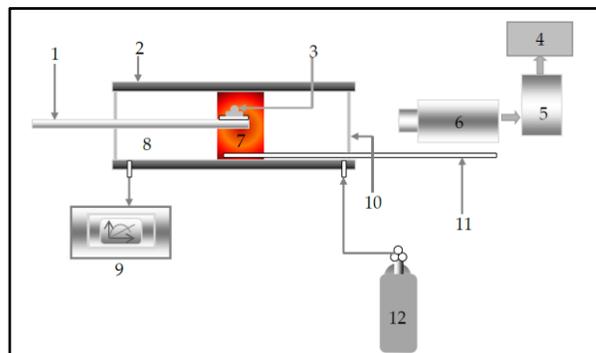


Fig. 3: Schematic of the horizontal tube furnace and IR gas analyser system. (1 Sample Rod; 2 Alumina tube; 3 Reaction mixture; 4 PC; 5 DVD; 6 CCD Camera; 7 Hot Zone; 8 Cold Zone; 9 Gas analyser; 10 Quartz window; 11 Thermocouple; 12 Argon gas)

The results (gas analyses and visual imaging) were recorded in a data-logging computer. The sample assembly was inserted in the furnace, which was purged continuously with argon (of 99.995 % purity and flowing at 1L/min) to ensure inert conditions in the furnace. After the furnace had attained the desired hot zone temperature (1520 °C), the sample was pushed into the reaction hot zone and the reactions were monitored for 30 minutes. This time was selected since initial trials showed that the reactions ceased and thus there were no further changes in gas composition or degree of reduction beyond this time. The 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 (**Fig. 4**), were removed magnetically and analysed.

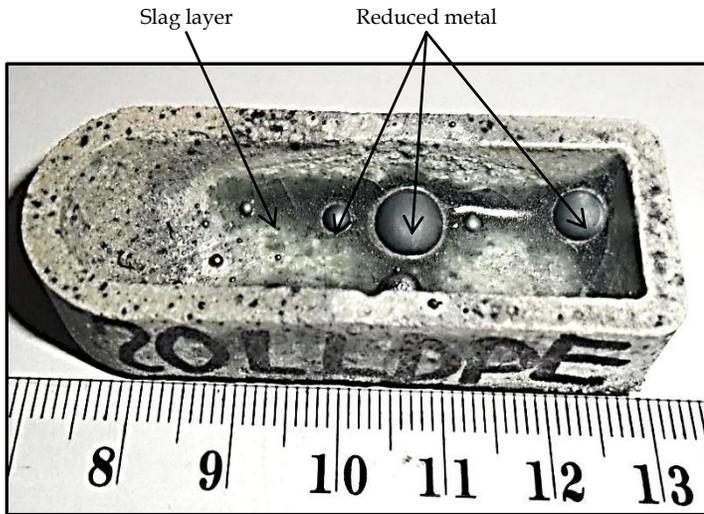


Fig. 4: Nature of metal produced from reduction of slag by Blend 2 at 1520 °C

3 RESULTS AND DISCUSSIONS

3.1 Gas generation rates (IR Analyser)

The contents of CO and CO₂ in the off-gas were measured continuously by an infrared (IR) gas analyser and the amounts of CO and CO₂ removed from the slag were calculated using the off-gas data for each blend. The results are shown in Figs. 5 and 6 for LLDPE and coke, respectively.

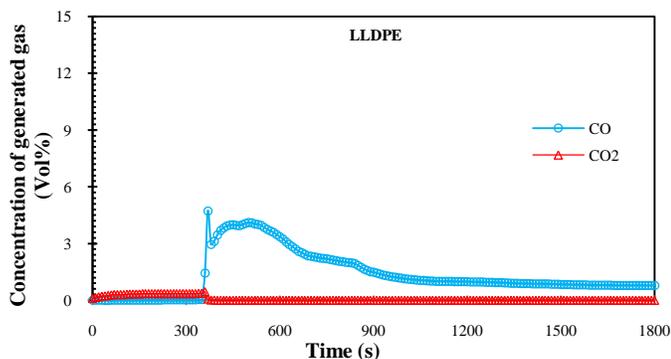


Fig. 5: Concentration of generated gas as a function of time during the reduction of FeO in slag by LLDPE at 1520 °C

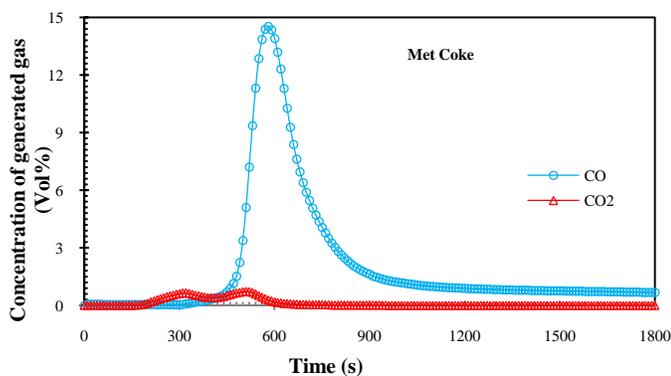
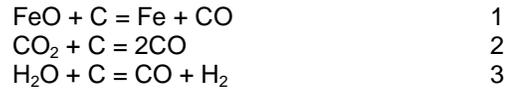
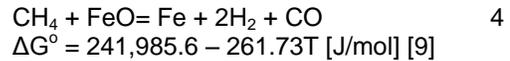


Fig. 6: Concentration of generated gas as a function of time during the reduction of FeO in slag by coke at 1520 °C

The relatively low values recorded for CO₂ compared to CO may be an indication of direct reduction of FeO by C (equation 1) or a dominant Boudouard reaction (equation 2) or carbon gasification reaction (equation 3).



Another possible reaction is the direct reduction of FeO by CH₄, which was the predominant hydrocarbon detected in the off-gas above 1500 °C.



3.2 Extent of reduction

The reduced metal, after ten minutes of reduction, was removed magnetically and 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 was determined from the oxygen values, bearing in mind that the initial concentration of removable oxygen from the reducible component of the slag (FeO) is about 22.27%. The result is illustrated in Table 5. From Table 5, the extent of reduction by coke was slightly higher than by LLDPE after ten minutes; blending with the polymer appears to improve reduction significantly with extent of reduction increasing consistently from 59.1% for coke to 86.5%, 89.8%, 94.6% and 94.9% for Blend 1, Blend 2, Blend 3 and Blend 4, respectively, and then declines to 50.5% for LLDPE. This improvement in reduction is attributed to the extra reducing gases H₂ and CH₄ made available in the system through the thermal decomposition of LLDPE. The beneficial effect of H₂ on the reduction of iron oxide by coke was elucidated in earlier investigation [3-5, 10-13].

TABLE 5: OBSERVED EXTENT OF REDUCTION FOR EACH CARBONACEOUS REDUCTANT

Reductant	Coke	B 1	B2	B 3	B 4	LLDPE
Extent of reduction (%)	59.1	86.5	89.8	94.6	94.9	50.5

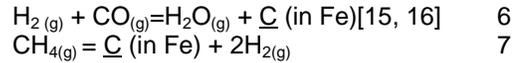
The observed improvement in extent of reduction with polymer addition is consistent with previous observations by Dankwah *et al.* (crucible reduction approach) [3-5], Rahman (sessile drop approach) [6], Zaharia *et al.* (sessile drop approach) [7] and Kongkarat (sessile drop approach) [14].

3.3 Content of carbon and sulphur in the produced metal

The contents of carbon and sulphur in the reduced metal were determined using a LECO carbon/sulphur analyser; the results are shown in Figs (7 and 8), for carburisation and sulphur removal respectively. Carburisation is lowest for the pure plastics (0.188 wt %), followed by metallurgical coke (0.650 wt %). The relatively low level of carburisation observed for the pure plastics compared to coke may be due to the absence of fixed carbon in the polymer. It increases consistently with the amount of LLDPE blended with coke; 3.115, 3.975, 5.107 and

5.360 wt % for Blends 1, 2, 3 and 4, respectively. The carburisation process for each of the blends is higher than either coke or LLDPE alone, indicating the existence of a favourable synergetic effect between coke and LLDPE towards carburisation of metallic iron as was observed in earlier investigations [3-5].

equation 5 and the following:



Fruehan[17] calculated an apparent rate constant for equation 6 that was over five times higher than that for equation 18. Kaspersma and Shay[18] determined the rate constant for carburization by equation 6 to be 16 times greater than that by equation 5 and 22 times that by equation 7. Karabelchtchikova [19] calculated a rate constant for equation 6 that was 30 and 100 times faster than equations 5 and 7 respectively. Therefore the rate of carburisation is expected to be significantly higher for the blends than for coke alone. The level of carburisation observed in this investigation is significantly higher than the marginal levels of carburisation observed by Kongkarat *et al.*, [20] who used the sessile drop approach. They observed a carburisation value of 0.1 wt % for the same metallurgical coke utilised in this investigation and 0.17 wt %, 0.15 wt % and 0.19 wt % for coke-HDPE, coke-PP and coke-bakelite blends having the same coke-polymer ratio as Blend 3 in the current investigation. The reason for the observed improvement in desulphurisation is not immediately apparent. "As was explained in the work of Dankwah *et al.* [3-5] a decrease in the time required for the complete melting of the slag was observed with an increase in the content of the polymer, up to 30 - 50 wt % polymer". Possibly, this improvement in the fluidity of the slag with polymer addition could promote the diffusion of calcium sulphide to the slag layer.



Using the sessile drop approach, Kongkarat [21] observed a reduction in sulphur pick up by iron when metallurgical coke was blended with bakelite, HDPE and PET in proportions similar to Blend 3 in the current investigation.

3.4 Environmental considerations (CO₂ evolution)

The relative amounts of CO₂ evolved after fifteen minutes reduction of the slag by LLDPE and coke were calculated and the results are plotted in Fig. 9.

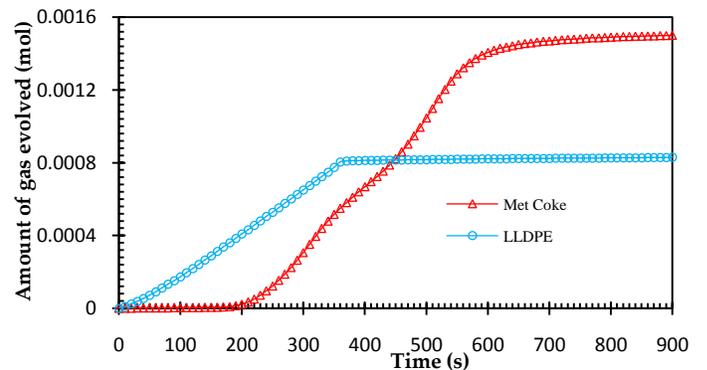


Fig. 9: Comparison of the accumulated amount of CO₂ generated from the reactions of the slag with LLDPE, and coke at 1520 °C

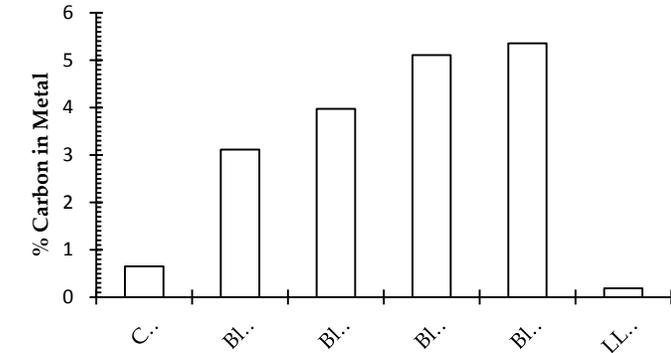


Fig. 7: Carburisation of the metal formed after reduction for each carbonaceous reductant at 1520 °C

The level of sulphur in the metal showed a reverse trend to that seen for carbon pickup, with the highest level of sulphur (0.177 wt %) found in the metal produced using pure metallurgical coke. The level of sulphur (0.149 wt %) found in the metal produced using pure LLDPE was lower than that of coke but was still significant. Blending resulted in significant decrease in the content of sulphur in the reduced metal with Blends 3 and 4 showing no values for sulphur content; this again indicates the existence of a favourable synergetic effect between coke and LLDPE towards the desulphurisation of metallic iron. Similar results were observed in earlier investigations [3-5].

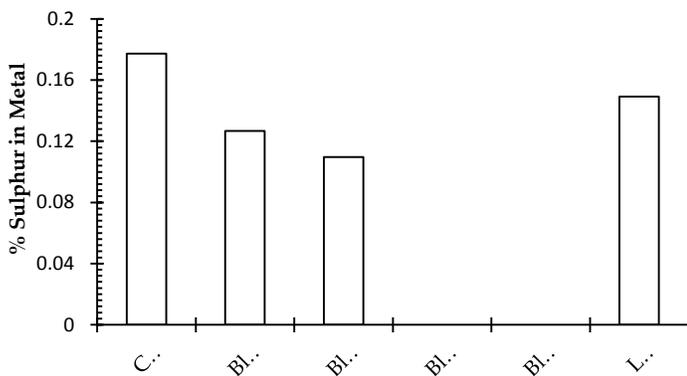


Fig. 8: Content of sulphur in the metal after reduction for each carbonaceous reductant at 1520 °C

The improved performance of the blends with respect to carburisation may be explained as follows: For pure metallurgical coke (no hydrogen present), the metal is carburised mainly by the reaction [15, 16]:



In a CO-H₂-CH₄ environment (due to thermal/catalytic cracking and gasification of the plastics) the produced metal is carburised via three parallel reactions, which consists of

It is clear from Fig. 9 that CO₂ emissions from coke were higher than from LLDPE; of course, these values correspond to CO₂ generation from the reduction reaction only; values do

not take into account the CO₂ evolved during the production of metallurgical coke from coal or the CO₂ generated to produce the electrical energy used to power the reduction process. The observed decrease in CO₂ emissions with LLDPE addition agrees with the observation by Matsuda et al [22] that it is possible to utilise waste plastics to produce metallic iron without generating CO₂.

4 CONCLUSIONS

The reduction of FeO from EAF slags by LLDPE and its blends with metallurgical coke has been investigated in a horizontal tube furnace at 1520 °C. The major findings of this investigation are:

- Blends of waste plastics (LLDPE) with metallurgical coke could be used to partly replace the conventional metallurgical coke used in ironmaking as reductant.
- Significant improvements in the extent of reduction were observed when metallurgical coke was partly blended with LLDPE. Extent of reduction increased from 59.1% (coke) to 94.9% (Blend 4)
- The degree of carburisation and desulphurisation of the reduced metal improved considerably when coke was blended with LLDPE. Whereas the content of carbon in the metal improved from 0.65 wt % for coke to 5.36 wt % for Blend 4 the sulphur content in the metal dropped from 0.177 wt % (coke) to 0 wt % (Blends 3 and 4)

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