

# Production of Metallic Iron from the Pudo Magnetite Ore using End-of-Life Rubber Tyre as Reductant: The Role of an Underlying Ankerite Ore as a Fluxing Agent on Productivity\*

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## Abstract

This research work investigated the nature of a nonmagnetic ore from Pudo in the Upper West Region of Ghana and its fluxing effect on the extent of reduction of the Pudo titaniferous magnetite ore using pulverised samples of charred carbonaceous materials generated from end-of-life vehicle tyres (ELT) as reductants. Reduction studies were conducted on composite pellets of the Pudo titaniferous magnetite iron ore containing fixed amounts of charred ELT and varying amounts (0%, 10%, 15%, 20%, 30%, 40% and 50%) of the nonmagnetic fluxing material in a domestic microwave oven and the extent of reduction was calculated after microwave irradiation for 40 minutes. Analyses by XRF and SEM/EDS of the nonmagnetic ore revealed an Ankerite type of ore of the form  $\text{Ca}_{0.95}\text{Fe}_{0.95}\text{Mn}_{0.1}(\text{CO}_3)_2$ . From the microwave reduction studies it was observed that premium grade metallic iron could be produced from appropriate blends of the Pudo iron ores using ELT as reductant, with a measured extent of reduction up to 103.8%. Further, the extent of reduction was observed to increase with an increase in the amount of the nonmagnetic fluxing material (Ankerite) that was added as fluxing agent.

**Keywords:** Ankerite, End-of-life Rubber Tyres, Fluxing Agent, Extent of Reduction

## 1 Introduction

The growing demand for automobiles and second-hand tyres has generated huge amounts of End-of-Life-Tyres (ELTs) in Ghana. In Ghana, unlike developed countries, ELTs are principally disposed in landfills or incinerated with little recycling approaches. Stockpiles of ELTs serve as ideal breeding grounds for mosquitoes and hiding places for reptiles such as snakes. This poses a significant health risk; fatal diseases such as malaria have been linked to such breeding grounds.

Moreover, stockpiles of these tyres can catch fire through lightning strikes or arson and such fires are notoriously difficult and costly to extinguish. Globally, about 1.5 billion ELTs make their way into the environmental cycle each year (Parthasarathy *et al.*, 2016).

The Pudo iron ore is one of the major iron deposits in Ghana. The ore is in the form of titaniferous – magnetiferous ore, containing both magnetite and titanium and a nonmagnetic type depending on its location (Kesse and Banson, 1975). The magnetite deposit has iron oxide ( $\text{Fe}_2\text{O}_3$ ) content of about 80 wt%. Chemical analyses by Kesse and Banson (1975) revealed the absence of phosphorus and an extremely low sulphur content.

Work done by Dankwah *et al.*, 2016 revealed that the nonmagnetic ore has an extremely low-grade

iron ore with a very high silica content and moderately high alumina content. Although the iron oxide content is very low, the ore is self-fluxing as evidenced by its high MgO and CaO contents. Besides, it has no sulphur and its phosphorus content is negligible; these features make the Pudo iron deposit a promising source of iron oxide for the production of metallic iron for the steelmaking industry in Ghana.

However, there are no known coal deposits in Ghana. It will be expensive to import coals or metallurgical coke for an Iron making industry in Ghana. The use of postconsumer plastics as reductants or as a source of energy is currently gaining the attention of various researchers in the metallurgical industry (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 *et al.*, 2013; Dankwah and Koshy, 2014; Dankwah *et al.*, 2015a; Dankwah *et al.*, 2015b). For thermosetting polymers and elastomers, Dankwah *et al.*, 2012, Mansuri *et al.*, 2013, Rajarao *et al.*, 2014a, Rajarao *et al.*, 2014b, Nath *et al.*, 2012, Dhunna *et al.*, 2014 and Dankwah and Baawuah, 2015 have used end-of-life rubber tyres, waste compact discs, end-of-life melamine and waste bakelite as reductants or for carbon dissolution studies.

More information is needed in the literature on the use of ELTs as reductants for the production of metallic iron from naturally occurring iron ores.

In this present work the potential for producing metallic iron from Pudo Magnetite ore using ELTs as a reducing agent and ankerite as a fluxing agent is investigated.

## 2 Resources and Methods Used

### 2.1 Materials

ELT(s) were collected from a tyre waste dump opposite the main gate of the University of Mines and Technology (UMaT), Tarkwa.

ELT(s) were cut into smaller sizes, washed, and dried. Dried samples were charred in a gas fired furnace for 20 min. The charred ELT(s) were pulverised using a standard laboratory ball mill to produce fine powders (-125 µm) of carbonaceous materials as shown in Fig 1.



**Fig. 1 Pulverised Sample of Charred ELT**

Two iron ores (titaniferous magnetite and nonmagnetic) (Fig. 2) were obtained from Pudo in the Upper West Region of Ghana.



**Fig. 2 (a) Pulverised Pudo Titaniferous Magnetite Iron Ore (b) Nonmagnetic Ankerite Ore**

### 2.2 Methods

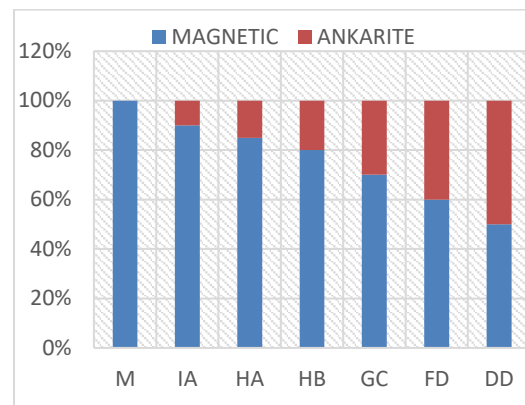
#### 2.2.1 Proximate Analysis of ELT(s)

Analysis for moisture, volatile matter, ash and fixed carbon contents were carried out on samples of the shredded ELT(s) using the ASTM D-7582-15.

#### 2.2.2 Reduction Studies

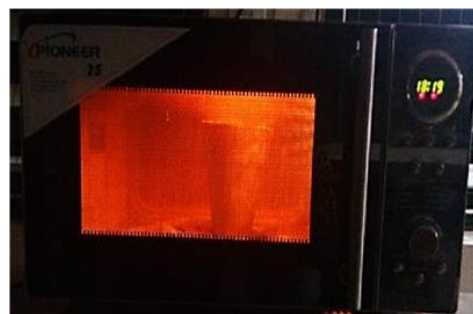
Spherical pellets were formed from pulverised iron oxide and charred ELT with a composition of 70% iron oxide (both magnetic and nonmagnetic), 28% of carbonaceous material and 2 wt% flour as binder and appropriate amount of water.

The blend composition for the iron ores is shown in Fig. 3



**Fig. 3 Blend Ratio of the Pudo Magnetic and Ankerite ores used in the Reducibility Studies**

After curing and drying for 96 hours the composite pellets were weighed using an electronic balance. The cured pellets were placed in a fireclay crucible and the crucible-pellet assembly was placed at the central position of a 2400 MW, 50 Hz, PIONEER domestic microwave oven as shown in Fig. 4. The composite pellets were irradiated for 40 min, after which the crucible was taken out and quenched in air to stop any further reactions. The weights of the reduced iron pellets were then recorded using an electronic balance.



**Fig. 4 Reduction Process in a Domestic Microwave Oven**

### 3 Results and Discussion

#### 3.1 Proximate Analyses of ELTs

The result of proximate analyses (ASTM D-7582-15) of the ELT(s) particles is revealed in Table 1. The volatile matter was the highest composition, which was recorded as 61.67 % followed by fixed carbon recorded as 29.88 %. The moisture and ash contents were noted as 0.85 and 7.60 % respectively. These values confirm studies done by various researchers on the proximate analysis of ELT(s) as shown in Table 1. The fixed carbon content of the ELT(s) is an indication that End-of-Life Rubber Tyres could be transformed into valuable substance, carbon black for carbothermal reduction processes.

**Table 1 Proximate Analysis of ELTs**

Author	Component (wt %)			
	Volatile	Fixed Carbon	Moisture	Ash
<b>This Research</b>	<b>61.67</b>	<b>29.88</b>	<b>0.85</b>	<b>7.6</b>
Juma <i>et al.</i> , (2006)	61.61	22.66	1.72	14.01
Rodrigues <i>et al.</i> , (2001)	58.8	27.7	-	3.9
Lee <i>et al.</i> , (1995)	67.3	28.5	0.5	3.7
Chang <i>et al.</i> , (1996)	62.32	26.26	1.31	10.29
Gonzales <i>et al.</i> , (2001)	61.9	29.2	0.7	8.0

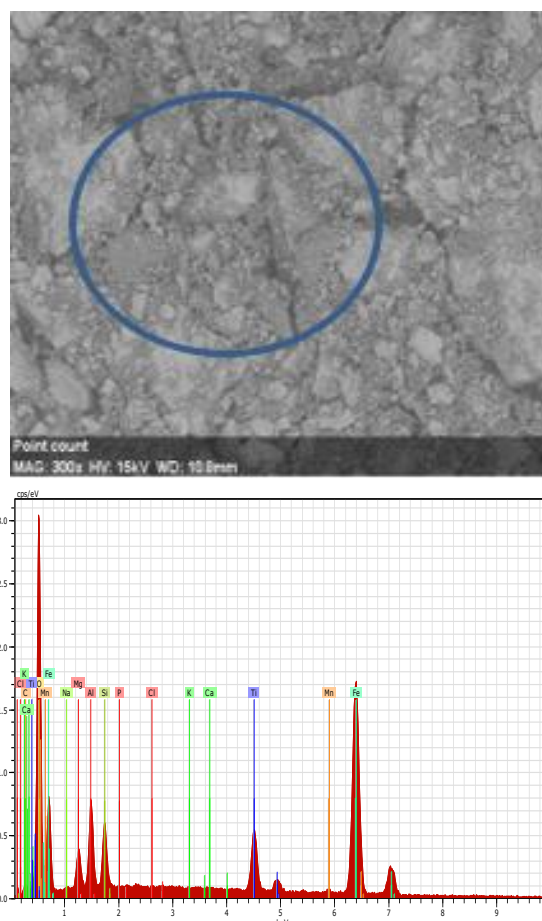
#### 3.2 Nature of the Pudo Iron Ores

The chemical composition (wt%) of the iron ores (determined by XRF analyses) at the Analytical Centre, UNSW, Australia is given in Table 2. From Table 2 it is seen that although the nonmagnetic ore has a very low iron oxide content, it is a self-fluxing ore owing to the presence of significant amounts of MgO, CaO and SiO<sub>2</sub>. The magnetic ore on the other hand has a very high iron oxide content with virtually no sulphur and phosphorus. This makes it a suitable candidate for metallic iron production.

The SEM/EDS analyses of the Pudo iron ores (magnetic and nonmagnetic) before reduction are illustrated in Figs. 4 and 5 and Table 3 and 4, respectively. These show the point-by-point surface analyses of the magnetite and nonmagnetic ore. It is apparent from Table 4 that the Pudo nonmagnetic ore consists of Ca, Fe, Mn, C, and O. From the atomic composition, the Pudo nonmagnetic ore can be represented by Ca<sub>0.95</sub>Fe<sub>0.95</sub>Mn<sub>0.1</sub>(CO<sub>3</sub>)<sub>2</sub>, implying an ankerite form of ore.

**Table 2 Chemical Composition (by XRF) of the Pudo Iron Ores used**

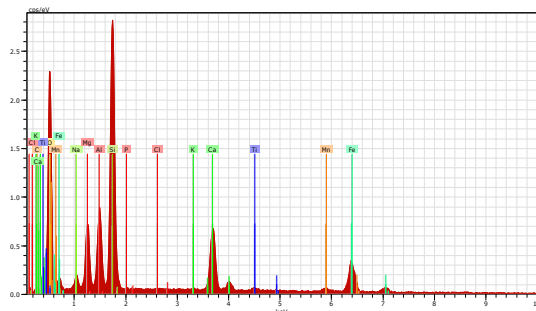
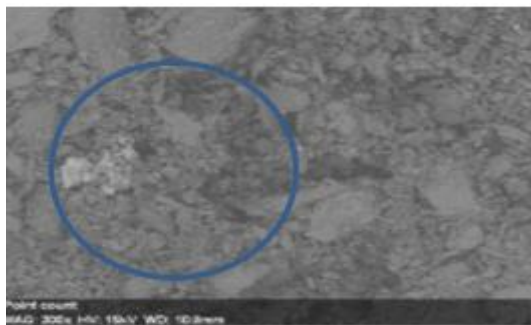
Component	Composition (wt %)	
	(Nonmagnetic)	Magnetic
Na <sub>2</sub> O	1.411	0.200
MgO	9.057	1.679
Al <sub>2</sub> O <sub>3</sub>	11.844	3.864
SiO <sub>2</sub>	47.244	2.519
P <sub>2</sub> O <sub>5</sub>	0.010	0.010
SO <sub>3</sub>	0.000	0.018
K <sub>2</sub> O	0.107	0.007
CaO	12.048	0.068
TiO <sub>2</sub>	0.947	10.140
Mn <sub>3</sub> O <sub>4</sub>	0.456	0.409
Fe <sub>2</sub> O <sub>3</sub>	14.958	80.918
LOI	1.96	1.16



**Fig. 4 SEM/EDS Analysis for Pudo Titaniferous Magnetic Iron Ore**

**Table 3 Values of SEM/EDs Analysis for Pudo Titaniferous Magnetic Iron Ore**

Element (K-Series)	Weight %	Atomic %
Fe	49.2	24.25
O	32.03	55.1
Ti	5.62	3.23
Al	4.15	4.23
C	3.13	7.18
Si	2.76	2.7
Mg	2.38	2.7
Mn	0.32	0.16
Na	0.31	0.37
Ca	0.1	0.07
<b>Sum</b>	<b>100</b>	<b>100.0</b>



**Fig. 5 SEM/EDs Analysis for Pudo Non-Magnetic Iron Ore**

**Table 4 Values of SEM/EDS Analysis for Ankerite Ore**

Element (K-Series)	Weight %	Atomic %
Fe	10.17	3.86
O	43.51	57.64
Si	20.08	15.15
Ca	7.30	3.86
Al	5.91	4.65
Mg	5.28	4.60
C	4.60	8.13
Na	1.56	1.44
Mn	1.02	0.39
Ti	0.35	0.15
P	0.01	0.01
<b>Sum</b>	<b>100</b>	<b>100</b>

Grades of Iron ore are classified according to their Fe content. An iron ore is said to be of high grade when its Fe content is more than 65 wt.%, low grade when its Fe content is less than 58 wt.%, and medium grade when its Fe content is between 58 wt.% and 64 wt.% (Kiptarus *et. al.* 2015; Muwanguzi *et. al.* 2012).

The potential for worldwide commercial exploitation of the Pudo iron ores is low but it is possible to exploit it on small scale basis. Comparing these values to the world's iron ore classification in Table 5 the Pudo magnetic iron ore corresponds to the low-grade iron ore (approximately 57 wt.% which is less than 58 wt.%).

**Table 5 Generalized Percentage Classification of Iron Ores**

Components	Total Iron Content		
	Low	Medium	High
Content Mass %	<58	62-64	>65

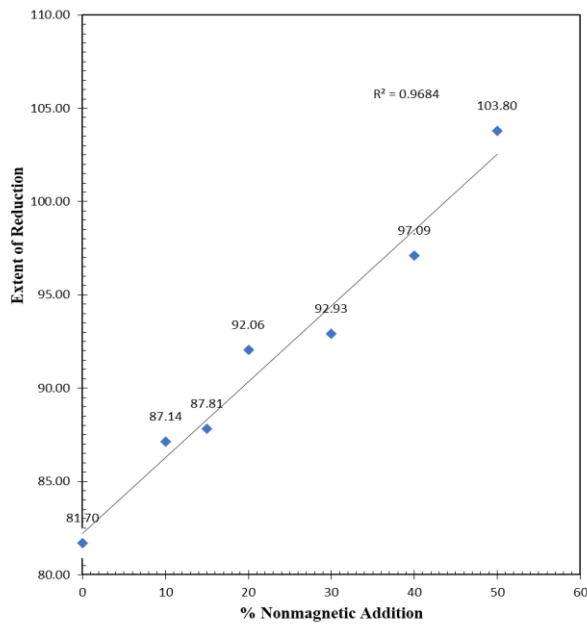
(Source: Kiptarus *et. al.* 2015)

### 3.3 Effect of Ankerite Addition on the Extent of Reduction

Fig. 6 shows the variation of extent of reduction with the content of ankerite in the pellet. The extent of reduction for the magnetic ore was 81.70%. The extent of reduction ranged a little over 87% to 103% for the various blends of the magnetic and ankerite ores.

The extent of reduction for the various blends increased with an increase in content of the non-magnetic ore in the composite pellet. This is because of the self-fluxing ability of the ankerite as explained earlier. CaO fluxes the gangue in the iron ore to form a silicate melt phase. MgO either enters the magnetite lattice to form magnesio ferrite or dissolves in the slag phase. These melting phases interact with each other and dissolve a variable amount of iron oxides.

The observed extent of reduction in excess of 100% is attributed to the simultaneous reduction of SiO<sub>2</sub> and the blend of the magnetite and non-magnetic ore to form an alloy of ferrosilicon.



**Fig. 6 Graph of Extent of Reduction for the Magnetite and Various Blends of the Magnetite and Nonmagnetic Ores**

### 3.4 Effect of Ankerite on the Nature of Metals Produced

It is observed from Fig. 7 below that direct reduced iron was produced. It has an irregular sponge-like structure. The reduced metal was formed in the solid state. The metallised portion of the DRI did not melt. This reduced pellet was the 100% magnetite-ELT composite pellet. It has a low metallisation because magnetite ores are naturally difficult to reduce to metallic iron because of its low porosity. Moreover, the Pudo magnetite ore is not a self-fluxing ore to enter into the molten state during reduction.



**Fig. 7 Samples of Reduced Material obtained after Reduction of 100% Pudo Magnetite Ore with ELT**

Fig. 8 illustrates the effect of 15% ankerite addition on the nature of metal produced from the Pudo magnetic ore.



**Fig. 8 Samples of Reduced Metal obtained after Reduction of Maximum Blend of 15% Ankerite Ore**

It can be observed from Fig. 8 above that blends with a maximum of 15% ankerite had irregular to spherical shape. They have higher metallisation than DRI due to the partial slag separation and reduced number of pores. This is because the ankerite ore served as a fluxing agent. Transition Direct Reduced Iron (TDRI) was produced as more carbon dissolved in DRI and the metallised portion partially melted as a result of the addition of the ankerite ore which served as flux.

Fig. 9 illustrates the nature of metal produced when the content of ankerite increased above 15%. The metals produced were spherical in nature. These spheres of metal were embedded in the slag phase of the reduced material and were subjected to breakage to free the spherical metals. Slag separation was achieved due to the formation of two liquid products; slag and metal. This is due to the immiscibility and density difference. The spherical shape of the metallic iron nuggets is an indication that they were solidified from the molten state. Physical separation of the mixture of reduced metals and slag components was effected using a low intensity handheld magnet. The spherical nature of the reduced metal could be attributed to the high CaO and MgO in the ankerite and the excess carbon present in the iron ore-carbon composite causing the reduced iron to pick up these excess carbons. This causes the reduced iron to melt at a lower temperature into a molten mass that solidifies into spherical nuggets when the microwave power is put off.



**Fig. 9 Samples of Reduced Metal obtained after Reduction of Blend Consisting of 50% Ankerite Ore**

#### 4 Conclusions

A laboratory investigation has been conducted on the nature of ankerite ore from Pudo and its fluxing effect on the extent of reduction of the Pudo titaniferous magnetite ore using pulverised samples of charred carbonaceous materials generated from end-of-life vehicle tyres (ELT) as reductants. Major findings of the investigation are:

- (i) ELTs are excellent potential source of carbonaceous material for iron oxide reduction.
- (ii) ELT utilised for this investigation has a fixed carbon content of 29.88% from its proximate analysis.
- (iii) The Pudo nonmagnetic ore is an ankerite type of ore of the form  $\text{Ca}_{0.95}\text{Fe}_{0.95}\text{Mn}_{0.1}(\text{CO}_3)_2$
- (iv) The Extent of reduction for the 100% magnetite ore was 81.70%; its metal had an irregular spongy-like structure.
- (v) Addition of ankerite to the Pudo magnetic ore resulted in an improvement in the extent of reduction and the quality of metal produced.

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