Waste Toner Powder, a Potential Resource for Iron and Steelmaking Technologies

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Dankwah, J. R., Anderson, M. and Owusu-Ansah, Y. (2022), "Waste Toner Powder, a Potential Resource for Iron and Steelmaking Technologies", *Proceedings of the 7th UMaT Biennial International Mining and Mineral Conference, pp 1 - 8.*

Abstract

Globally, an estimated 1.1 billion printer toner cartridges are sold each year with over 500 million of these ending up in landfills. In this work the potential for recovering iron oxide and carbonaceous materials from waste toner powder is demonstrated through the iron oxide-carbon composite pellet approach. Composite pellets of low-grade nonmagnetic iron ore (sourced from Pudo in the Upper West Region of Ghana) were formed with measured samples of waste toner powder obtained from printing presses on UMaT campus. Reduction studies were then conducted on the cured, sufficiently dry pellets in a domestic microwave oven (Pioneer, Model PM-25 L, 1000 W, 2.45 GHz). Reaction products were characterised by SEM/EDS and XRD analyses and the extent of reduction after 40 min was determined. XRD, XRF and SEM/EDS analyses showed that the waste toner ore consists of spherical samples of magnetite (assaying ~34.2 wt % Fe_2O_3) and excess carbonaceous materials (assaying ~ 58.75 wt.% to 70.19 wt.% C) for complete reduction of the ore-toner composite pellet. Ashed samples of the waste toner samples revealed iron oxide contents ranging from 80.1 wt% to 84.4 wt% Fe_2O_3. Further, mass balance on the total removable oxygen from the composite pellet and the reduced metal showed that up to 97.6 wt% of the iron could be recovered from the ore-toner mixture. Waste toner powder is therefore a potential source of iron oxide and carbon for iron and steelmaking technologies.

Keywords: Reduction; Pudo Iron Ore; Toner Powder; Extent of Reduction

1 Introduction

E-waste is a waste generated from discarded electrical and electronic gadgets such as discarded printers, photocopiers and fax machines, which make use of toner powder for recreating texts and images. Globally, millions of tonnes of this waste stream are produced annually. It is estimated that about 1.1 billion cartridges are sold annually, with over 500 million units ending up in landfills across the world (Gaikwad *et al*., 2017), resulting in the pollution of the environment due to leaching of toxic chemicals (Gaikwad *et al*., 2017). This residual toner powder has fine particles which are combustible and capable of increasing the risk of dust explosion if it is airborne (Koseki 2014). An end-of-life toner cartridge is estimated to contain about 8% by weight of the residual toner powder (Ruan *et al*. 2011). This translates to approximately 0.697 kg waste toner powder per end-of-life toner cartridge (or ~350 metric tonnes of waste toner) disposed of annually in landfills and its consequential environmental impact.

Strict environmental requirements (from various environmental agencies across the globe) have placed the onus on most manufactures to offer programs for waste toner powder at a fee. However, due to the high cost associated with end-of-life toner recycling processes, most consumers tend to improperly dispose of this waste into mixed municipal solid waste streams (Yordanova *et al.*, 2014).

Waste toner powder is complex mixture of:

- iron oxide,
- carbon black (which serves as pigment),
- polymethyl methacrylate (PMMA) $(C_5H_8O_2)_n$,
- amorphous silica whose function is to serve as an additive,
- pigments (titanium hydroxide),
- polypropylene $(C_3H_6)_n$,
- waxes,
- styrene acrylate copolymer $(C_8H_8.C_3H_4O_2)_n$ and

- some specific metal salts whose function is to control the electromagnetic properties (Ewers and Nowak, 2006).

Work done by Tripathi *et al.* (2000) showed that single component toners are comprised of 40 to 50% styrene-acrylate copolymer (Fig. 1), 40 to 50% iron oxide and a small amount of carbon black and other ingredients. This range of composition makes single toner powders potential feedstock for ironmaking and steelmaking technologies. Whereas the iron oxide is an excellent source of iron, the polymer (styrene-acrylate copolymer) and carbon black could function as reductants for the ironmaking step.

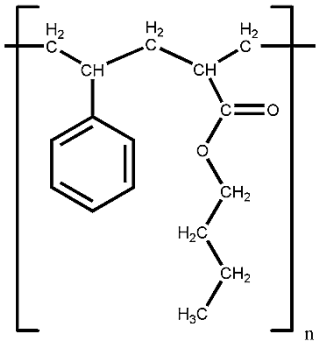


Fig. 1 Structure of styrene butyl acrylate copolymer

Owing to their extremely fine particle size (~2 to 10 µm) and their highly hydrophobic nature (Ewers and Nowak, 2006), mixing them with equally sized iron ores and other carbonaceous materials for pellet formation is problematic.

Measures have been proposed by other investigators to deal with the large quantities of waste toner powder that are discarded annually. These include:

- Tripathi *et al.* (2000) produced toner modified asphalt cement by blending end-of-life toner powder with asphalt; the resulting product displays unique properties like higher temperature resistance and improved strength compared to the unmodified asphalt concrete used in road construction
- Yordanova *et al.* (2014) utilised end-of-life toner powder as fillants and colorants in synthetic rubber production.
- produced synthetic oils, gases, nano-Fe_3O_4 and nano-SiO_2 from end-of-life toner powder by utilising vacuum gasification condensation [Gaikward *et al.* (2014); Ruan *et al.* (2011a); *et al.* (2011b); Ruan *et al.* (2012); Ruan *et al.* (2013); Ruan *et al.* (2017)]
- Li *et al.* (2017) investigated the heat treatment of waste toner powder and its subsequent utilisation as an anode in Lithium ion batteries.

From the toxicological point of view, two of the components in toner (carbon black and titanium hydroxide) have been classified by the International Agency for Research on Cancer (IARC) as 'possibly carcinogenic to humans' (Group 2B) (Yordanova *et al.*, 2014).

It is apparent from the foregoing discussions that several interventions have been made by researchers, all aimed at finding a solution to the environmental issues associated with end-of-life toner powder. More research is still needed in this area since the amount of toner cartridges that is discarded annually is not declining. Accordingly, in this research, the utilisation of end-of-life toner powder as potential feedstock in ironmaking and steelmaking technologies is investigated.

2 Materials and Methods Used

2.1 Material Preparation and Characterisation

Samples of end-of-life toner powder were gathered from the two printing presses in the two main halls of the University of Mines and Technology, Tarkwa. Owing to the extremely high hydrophobic nature of the toner powder, reagent grade sodium carbonate (> 99.0 wt. % Na_2CO_3) was procured from Sigma-Aldrich to assist in the pellet formation step. A portion of the end-of-life toner powder (Fig. 2) was characterised by Scanning Electron Microscopy coupled with Energy-Dispersive Spectroscopy (SEM/EDS, Carl Zeiss EVO MA15) at the Environmental Monitoring Laboratory of the University of Mines and Technology, Tarkwa. The essence of this characterisation was to study the morphology and composition of the ultrafine toner powder.

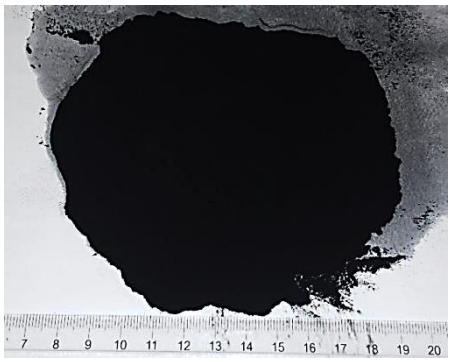


Fig 2 Sample of Waste Toner Powder used for the Experimental Investigation

2.2 Ashing of the End-of-Life Toner Powder

About 200 g of raw toner powder was placed in a fireclay crucible and the crucible was fired continuously on a charred palm kernel fired furnace for 40 min (Fig. 3). The crucible was allowed to cool sufficiently and its content was emptied into a metal bowl. The ashed sample was then weighed and the % weight loss was determined. Part of the ashed sample was submitted for XRF analysis.

Fig. 3 Firing of Crucibles containing End-of-life Toner Powder.

2.3 Reduction Studies (Composite Pellet Approach)

The suitability of end-of-life toner powder as reductant for iron oxide reduction was assessed here. The Pudo magnetiferrous titaniferrous ore was used as the source of iron oxide.

2.3.1 Formation of Iron Ore-Waste Toner Composite Pellets

Iron ore-toner composite pellets were formed by mixing 62.69 g of the ore with 37.31 g of end-of-life toner powder. About 1.52 g of pulverised $NaCO_3$ was added to the mixture to overcome the highly hydrophobic nature of the toner powder. Spherical pellets (Fig. 4) were formed by adding controlled amounts of distilled water to the mixture followed by hand rolling.

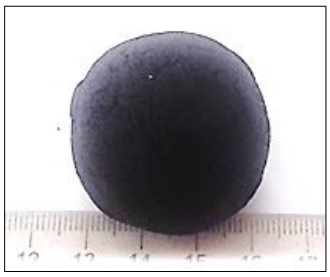


Fig. 4 Green Iron Ore-Toner Composite Pellet before Firing

The composite pellets were allowed to dry in open air for a minimum of 96 hours to allow for sufficient curing and drying.

2.3.1 Reduction Studies (Microwave Approach)

The reducibility of the iron ore-waste toner composite pellets was investigated in a domestic microwave oven (Pioneer, Model PM-25 L, 1000 W, 2.45 GHz) as shown in Fig. 5.

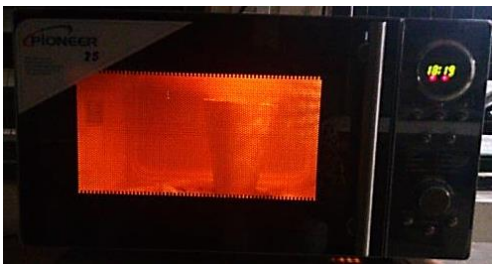


Fig. 5 Firing of Iron ore-Waste Toner Composite Pellets in a Domestic Microwave Oven

Each composite pellet was weighed before being placed in a fireclay crucible. The crucible-pellet assembly was then position a carefully located point in the domestic microwave oven to ensure maximum irradiation of the pellet. Each composite pellet was irradiated for 40 mins, after which the oven was switched off and the crucible removed and quenched in water to prevent re-oxidation of the reduced pellet in air. The reduced pellet was weighed again, followed by characterisation through XRD and SEM/EDS analyses.

3 Results and Discussion

3.1 FTIR Analysis of Waste Toner Powder

The toner powder utilised for the present investigation is a mixture of different types of toners. Accordingly, complete identification of the various polymeric components would be a difficult task. However, it is possible to identify various functional groups present in the toner powder by means of FTIR spectroscopy. This can help in determining the types of polymers present in the sample. Fig. 6 shows the FTIR spectrum of the waste toner powder.

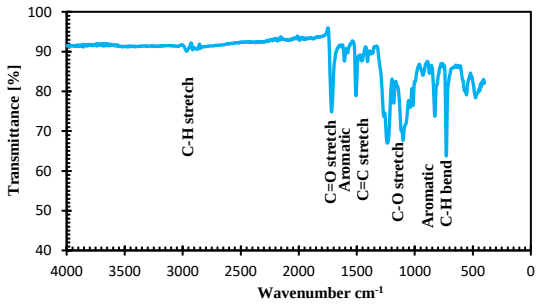


Fig. 6 FTIR Spectrum of the Waste Toner Powder utilised for this Investigation

The peak at 754.17 cm^{-1} along with those at 1606.25, and 2846.57 and 2913.86 cm^{-1} are indicative of the presence of polystyrene (PS). Specifically, the peak at 754.17 cm^{-1} can be attributed to C−H out-of-plane bending vibration. Aromatic C=C stretching vibrations are manifested in the 1606.25 cm^{-1}. The peaks 2846.57 and 2913.86 cm^{-1} can be attributed to the aliphatic C−H stretching vibrations from the CH_2 groups (Asis *et al.*, 2012; Kaniapan and Latha 2011; Gaikward, 2017). The presence of acrylic resins such as poly(methyl methacrylate) (PMMA) is suggested by the peaks at ~2966.53, 1717.28, 1457.66, and 1181.81 cm^{-1}. The peaks around ~2966−2914 cm^{-1} could be attributed to C−H stretching vibrations from the CH_3 and CH_2 groups, and the peak at 1717.28 cm^{-1} is due to the C=O (carbonyl) stretch (Choi *et al.*, 2001). The peak at 1457.66 cm^{-1} may be due to the C−H bending vibration of a CH_3 group (Shneider *et al.*, 1979; Duan *et al.*, 2008; Gaikward, 2017). The C−O−C stretching vibration is exhibited in the peak at ~1182 cm^{-1} (Asis *et al.*, 2012; Duan *et al.*, 2008; Gaikward, 2017; Torikai *et al.*, 2012). In addition, the peaks at 1507.56 and 827.73 cm^{-1} are suggestive of the presence of a bisphenol A-based polymer, such as polyester (Gaikward *et al.*, 2017; Mitchell *et al.*, 2013). On the basis of the FTIR analysis, the polymeric component of the waste toner powder sample is predominantly a PS−PMMA-type copolymer along with some bisphenol A-based polyester resin.

3.2 SEM-EDS Analyses

SEM micrographs for the waste toner powder are shown in Figs 7-8 at two different magnification levels. The morphology is dominated by spherical particles with diameters of ~5−10 µm, which could be components of the toner powder (including pigments such as magnetite and manganese oxide) encapsulated by resin particles of PS and PMMA. This metal oxides-polymer arrangement could be the reason for the hyper hydrophobicity observed during the pellet formation process. The toner powder utilised for this investigation can therefore be viewed as consisting of numerous micro-pellets of iron oxide−carbon composites having a core−shell structure (Gaikward *et al.* 2017). The core consists predominantly of magnetite, which is encapsulated by a carbon-rich shell of polymeric pair PS−PMMA (Gaikward *et al.* 2017).

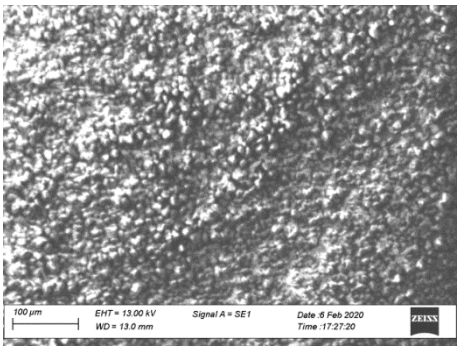


Fig. 7 SEM Micrograph of the Waste Toner Powder utilised for this Investigation

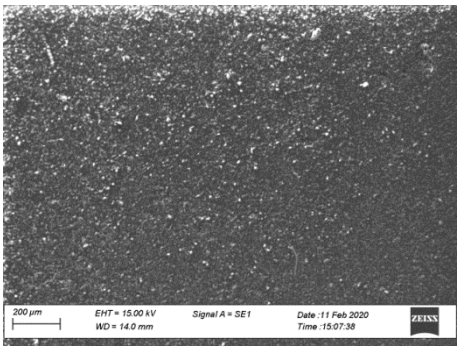
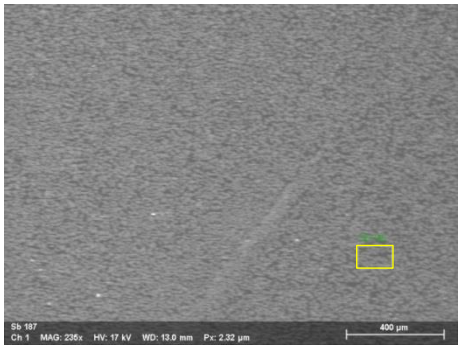
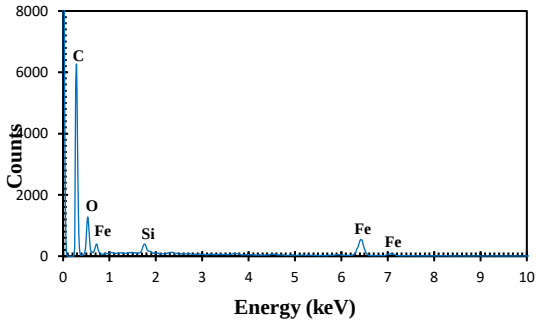


Fig. 8 SEM Micrograph of the Waste Toner Powder utilised for this Investigation

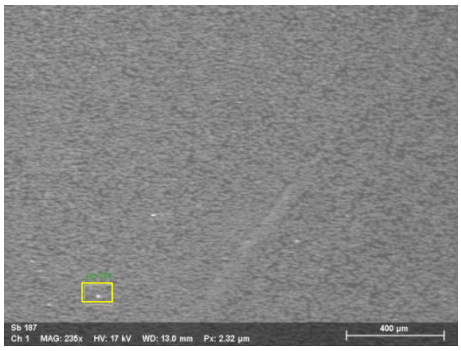
Figs 9-12 illustrate point by point analyses of four different regions in the micrograph of the waste toner powder. The major component is carbon, which ranges from a composition of 58.75 wt.% to 70.19 wt.%, followed by oxygen (22.29-24.86 wt.%), iron (4.42-17.37 wt.%), silicon (0.54-1.24 wt.%) and minor amounts of manganese (ca. 0.69 wt.%) and calcium (ca. 0.35 wt.%). Hence, the SEM-EDS mapping of the toner powder demonstrate the predominance of carbon, along with some clusters of Fe_3O_4 particles and SiO_2, which is added as charge control agent to prevent aggregation of the particles. Minor amounts of oxides of manganese and calcium were also observed.

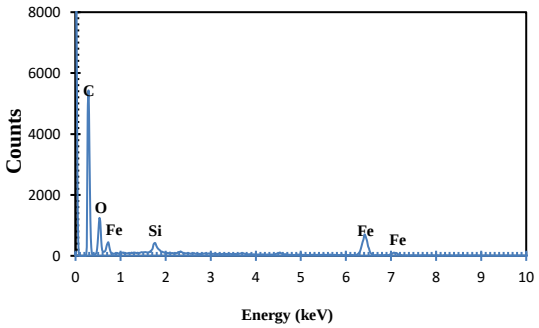




Element	Mass [%]	Atom [%]
C	62.04	74.94
O	23.09	20.94
Fe	12.97	3.37
Si	0.87	0.45
Mn	0.69	0.18
Ca	0.35	0.13
SUM	100	100

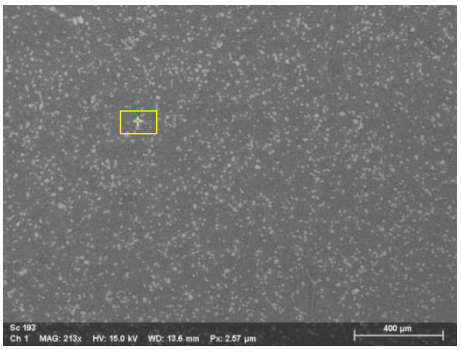
Fig. 9 SEM/EDS of the Waste Toner Powder utilised for this Investigation (Region 1)

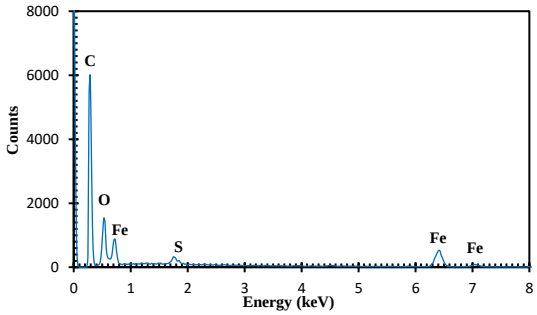




Element	Mass [%]	Atom [%]
C	60.78	74.65
O	22.29	20.56
Fe	15.69	4.15
Si	1.24	0.56
SUM	100	100

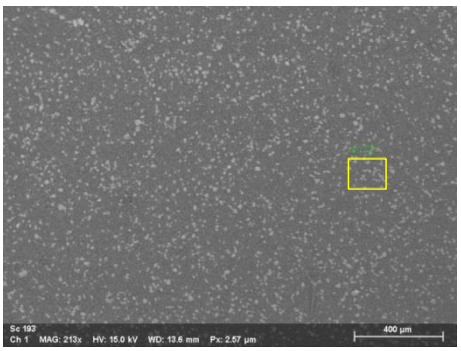
Fig. 10 SEM Micrograph of the Waste Toner Powder utilised for this Investigation (Region 2)

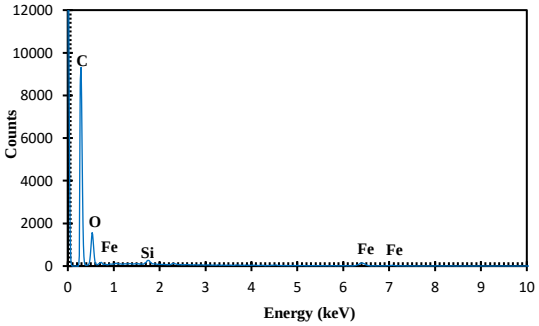




Element	Mass [%]	Atom [%]
C	58.75	73.22
O	23.33	21.83
Fe	17.37	4.66
Si	0.54	0.29
SUM	100	100

Fig. 11 SEM Micrograph of the Waste Toner Powder utilised for this Investigation (Region 3)



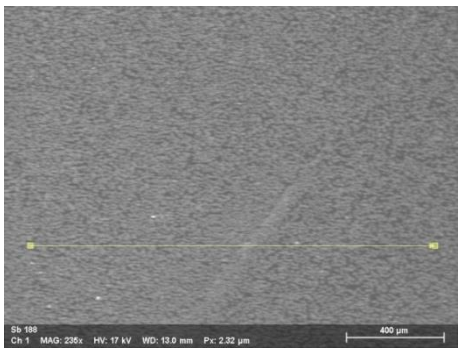


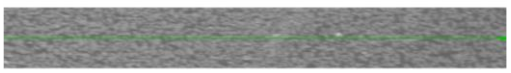
Element	Mass [%]	Atom [%]
C	70.19	77.96
O	24.86	20.73
Fe	4.42	1.06
Si	0.54	0.25
SUM	100	100

Fig. 12 SEM Micrograph of the Waste Toner Powder utilised for this Investigation (Region 4)

3.3 Line Scan Analyses

Results of line scan analyses of the SEM micrograph are illustrated in Fig. 13 and Fig. 14. Both reveal high levels of carbon along with iron, oxygen, silicon, manganese and calcium, again suggesting the presence of Fe_3O_4, SiO_2 and MnO, CaO along and across the SEM micrograph.





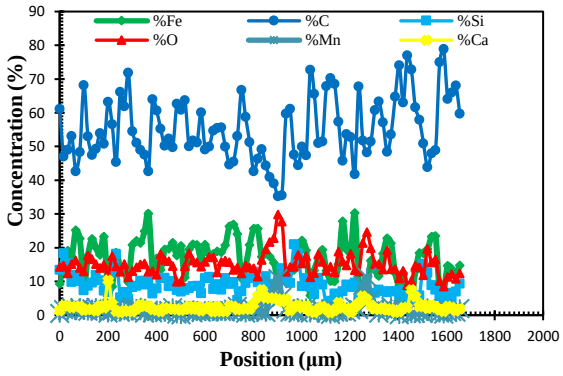
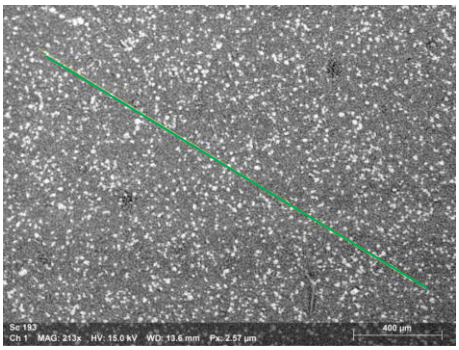
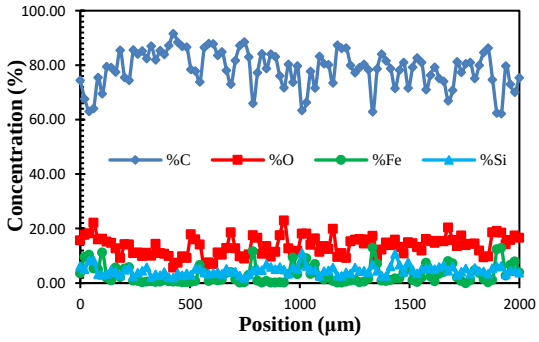


Fig. 13 Line Scan Analysis (Line 1) of the SEM Micrograph of the Waste Toner Powder utilised for this Investigation





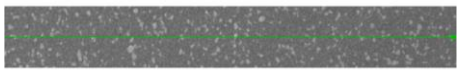


Fig. 14 Line Scan Analysis (Line 2) of the SEM Micrograph of the Waste Toner Powder utilised for this Investigation

3.4 Composition of Toner Powder Ash

Three samples of toner ash powder were ashed and characterised by XRF analysis. The results are shown in Table 1. Significant amounts of iron oxide, ranging from 80.1 wt% to 84.4 wt% Fe_2O_3

can be observed in all the three ashed samples of the toner powder, similar to earlier observation by Gaikward *et al.*, (2017). It is worthy of note that, besides the high levels of Fe_2O_3, all the ash samples contain appropriate amounts of MgO, CaO, Al_2O_3, SiO_2 and P_2O_5 for iron and steelmaking purposes. Although, the contents of SO_3 and TiO_2 are a bit on the higher side, they do not appear to exceed threshold levels for iron and steelmaking technologies. Waste toner powder is therefore a resource that could be added iron oxide ores destined for iron and steelmaking technologies, as it contains significant amounts of carbon and iron oxide for such purposes.

Table 1 Analyses by XRF of three Ashed Samples of Toner Powder

Component (wt %)	Ash 1	Ash 2	Ash 3
MgO	1.870	3.028	3.016
Al_2O_3	3.845	3.909	3.132
SiO_2	4.466	3.003	1.546
P_2O_5	0.155	0.120	0.120
SO_3	0.943	0.770	2.734
K_2O	0.251	0.460	0.050
CaO	1.984	1.093	1.366
TiO_2	4.623	1.735	3.321
MnO	0.313	0.424	0.133
Fe_2O_3	80.076	83.568	84.440
V_2O_5	0.008	0.008	0.099
Cr_2O_3	0.175	0.130	0.028
Rb_2O	0.006	0.005	0.008
SrO	1.256	1.730	0.000
Y_2O_3	0.000	0.000	0.002
ZrO_2	0.009	0.004	0.000
Nb_2O_5	0.007	0.004	0.000
SnO_2	0.012	0.008	0.000
U_3O_8	0.000	0.000	0.007
TOTAL	**100**	**100**	**100**

3.5 Results from Reduction Studies

Samples of metallic iron obtained from the reduced pellet in the domestic microwave oven are shown in Fig. 15.

Fig. 15 Samples of Metallic Iron Produced from Heating Composite Pellet of Pudo Iron Ore with Waste Toner Powder

It is seen from Fig. 15 that the iron ore–waste toner powder mixture is an excellent microwave energy absorber; this is evidenced by the large amounts of spherical iron nuggets that suggest that the metals were formed in the molten state. Even in the situation where the metal is highly carburised or alloyed with other elements (Si, Mn, Ti, etc.), temperatures in excess of 1150 °C are expected. Measured extent of reduction of up to 97.6% was observed.

4 Conclusions and Recommendations

Raw and ashed samples of waste toner powder were characterised by FTIR, SEM/EDS and XRF analyses to ascertain their usefulness as chemical feedstock for iron and steelmaking technologies. Portions of waste toner powder were mixed with samples of the Pudo iron ore, from which composite pellets were formed and irradiated in a domestic microwave oven for 40 mins. It was concluded that:

i) Waste toner powder is a rich source of carbon, polymers and Fe_3O_4 that could serve as chemical feedstock for iron and steelmaking technologies;

ii) Ashing the toner powder improved its iron oxide content to between 80.1 to 84.4 wt% Fe_2O_3;

iii) Irradiation of composite pellets of the Pudo iron ore with controlled amounts of waste toner powder in a domestic microwave oven resulted in the production of highly reduced metallic iron, with extent of reduction up to 97.6%.

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