

Calcination Behaviour of Guizhou Siderite Ore and its Amenability to Reduction by Waste Polymers*

¹P. Koshy, ²J. B. Dankwah, ³J. Dankwah and ²J. R. Dankwah

¹University of New South Wales, Sydney, Australia

²University of Mines and Technology, Post Office Box 237, Tarkwa, Ghana

³Goldfields Ghana Limited (Damang Mine), Tarkwa, Ghana

Koshy, P., Dankwah, J. B., Dankwah, J. and Dankwah, J. R. (2018), "Calcination Behaviour of Guizhou Siderite Ore and its Amenability to Reduction by Waste Polymers", *Ghana Journal of Technology*, Vol. 3, No. 1, pp. 63 - 68.

Abstract

Siderite (FeCO₃) ore from Guizhou, China was heated for 40 mins in air in the absence and presence of high density polyethylene, HDPE, (sourced from waste pure water sachets) in a horizontal tube furnace and gas fired furnace. Solid reaction products were characterised using XRF, XRD and SEM/EDS analyses whilst gaseous products were analysed by a continuous infrared gas analyser. Composite pellets of the calcined product with HDPE were then heated in a gas fired furnace for 40 mins and the product was analysed by XRD and SEM/EDS analyses. The solid products after calcination were found to be highly magnetic with composition by XRF of 95.82 wt % Fe₂O₃, 2.95 wt % SiO₂, 0.254 wt % Al₂O₃ and LOI of 0.40 wt % compared with an original XRF composition of 51.43 wt % Fe₂O₃, 10.80 wt % SiO₂, 9.46 wt % Al₂O₃ and LOI of 24.75 wt %. Analysis by XRD revealed maghemite (γ-Fe₂O₃) and magnetite (Fe₃O₄) as the predominant components of the calcined product from microwave irradiation and gas fired furnace, respectively, compared to FeCO₃, SiO₂ and Al₂O₃ for the original ore. Gas analysis by the IR gas analyser showed CO₂ and CO as the major components in the off gas in the ratio of CO₂/CO of approximately 2.0 when heated in the absence of the waste polymer. Heating in the presence of the waste polymer resulted in a drastic reduction in the composition of CO₂ from an accumulated amount of 1.396 × 10⁻² mol to 7.512 × 10⁻³ mol after 15 mins, with a corresponding increase in the content of gaseous reductants (CO, CH₄ and H₂) in the off gas. Metallic iron and syngas (CO + H₂) were observed to be the main solid and gaseous products after reduction of the calcined product.

Keywords: Calcination, Siderite ore, Reduction, Waste polymers, Microwave Irradiation

1 Introduction

Siderite (FeCO₃) is an important mineral which finds application in various industries and has gained commercial importance over the years (Dhupe and Gokarn, 1990). It is one of the main sources of iron in Europe (Fedorenko *et al.*, 1973) and is preferred to limonite as a raw material in cement industries, mainly because the reaction activity of siderite with lime has been found to be better than that of limonite (Hong and Myong, 1976). In iron and steelmaking technologies, siderite ores can be upgraded by controlled calcination of nonmagnetic FeCO₃ to magnetic Fe₃O₄ or γ-Fe₂O₃ followed by magnetic separation using a low intensity magnet of magnetic strength 0.17 T. However, this transformation depends on the partial pressure of oxygen, and consequently, on the furnace conditions. Microwave heating of siderite ore is advantageous for subsequent magnetic separation (Znamenáčková *et al.*, 2005). On calcination, grains of siderite become porous and accordingly become a good candidate for hydrogen production by the steam-iron process and probably for SO₂ pollution abatement (Chatterjee *et al.*, 1980, Dhupe *et al.*, 1987). Znamenáčková *et al.* (2005) investigated the microwave calcination behaviour of siderite ore from Nižná Slaná, Slovakia. They observed in a low intensity

magnetic field that the magnetic separation of heated samples showed a rapid growth of Fe recovery equal to 84.4% and 97.6% into magnetic products after 10 and 15 min of microwave irradiation, respectively. They observed further that magnetic susceptibility (κ) of untreated FeCO₃ increased from 947 × 10⁻⁶ to 28 736 × 10⁻⁶ and 140 870 × 10⁻⁶ after 10 and 15 min of microwave irradiation, respectively.

Alkaç and Atalay (2008) studied the kinetics of thermal decomposition of Hekimhan-Deveci siderite ore. They measured apparent activation energies of 85.53 kJ/mol and 85.49 kJ/mol based on the Jander and Ginstling-Brounshtein three dimensional diffusion models, respectively.

The experimental condition needed to fully understand the mode of calcination is difficult because extremely low partial pressures of oxygen are required to maintain the reduced oxides of iron in the temperature region of interest (Gallagher and Warne, 1981). Besides, wustite (FeO) is unstable below 563 °C and may disproportionate into iron and magnetite (Fe₃O₄) in accordance with equation 1:



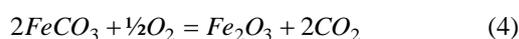
Accordingly, three mechanisms are currently in place to explain the mechanism of calcination of siderite. The first mechanism assumes that the decomposition product is wustite and any magnetite that appears is based upon a reaction with the atmosphere, which may include its own decomposition product (Gallagher and Warne, 1981), as illustrated in equation (2):



The second mechanism assumes that thermodynamic equilibrium is established during the bond breaking process associated with the decomposition and that no wustite is formed, as illustrated in equation (3).



The third mechanism assumes that in the presence of atmospheric oxygen the reduced oxide and any CO formed would be immediately oxidised as shown in equation (4).



Having an idea about which of the mechanisms control the calcination process is crucial to the overall upgrading of the ore by magnetic separation.

The aim of this investigation is therefore to establish a fundamental understanding of the calcination behaviour of the Guangzhou siderite ore and the amenability of the calcined ore to reduction by waste plastics.

2 Resources and Methods Used

2.1 Materials

Naturally occurring siderite ore from Guangzhou, China with composition shown in Table 1, was used for this experimental investigation as a source of $FeCO_3$, whilst samples of pure water sachets (PWS) collected from the university of Mines and Technology, Tarkwa were used as the source of reductant.

Table 1 XRF of Pulverised Siderite Ore before Calcination

Component	SiO ₂	Al ₂ O ₃	MgO	Mn ₃ O ₄	TiO ₂
wt %	10.795	9.462	1.403	0.428	0.383
Component	CaO	Fe ₂ O ₃	SO ₃	Other oxides*	LOI
wt %	0.813	51.432	1.835	0.492	24.75

*Other oxides: Na₂O, K₂O, P₂O₅, ZrO₂, Cr₂O₃, V₂O₅, ZnO, CuO,

PWS were shredded using a pair of scissors and thoroughly cleaned by rinsing with water in a plastic container to remove most of its associated

debris (Dankwah *et al.*, 2016). The cleaned PWS were thereafter air-dried for two days after which pulverised (-180 μm) carbonaceous materials were prepared through a heating-quenching sequence in a manner described elsewhere (Dankwah *et al.*, 2015)

2.2 Experimental Procedure

2.2.1 Calcination of Guangzhou Siderite Ore

Approximately 50 g of pulverised (-75 μm) Guangzhou siderite ore was placed in a fireclay crucible and calcined for 40 mins in a gas fired furnace. The calcined sample was quickly withdrawn from the furnace and the temperature was recorded using a K-type thermocouple; the calcined sample was then allowed to cool and its mass measured and recorded using an electronic balance (Ohaus PA214 Pioneer Analytical of capacity 210 g). This procedure was repeated three times after which the calcined samples were crushed, ground and sieved to -75 μm.

Thereafter, about 2.0 g of the ore was compacted in a die to produce cylindrical pellets (~1.2 mm thick and 15 mm diameter) (Fig. 1), by applying a load of 7.5 tonnes for 2 minutes in a hydraulic press. Each cylindrical pellet was placed in LECO™ crucible and the sample assembly was inserted in the cold zone of an electrically heated horizontal tube furnace (Fig 2), which was purged continuously with argon (of 99.995% purity and flow rate 1.0 L/min) to ensure inert conditions.

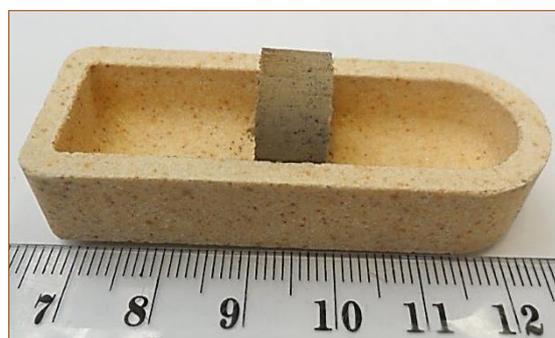


Fig. 1 Cylindrical Pellet of Guangzhou Siderite Ore in a LECO™ Crucible

After the furnace had attained the desired hot zone temperature (1150 °C), the sample was pushed in the reaction hot zone and gases (CH₄, CO and CO₂) were monitored for 900 s by an infrared gas analyser attached to the system; the results were recorded in a data-logging computer.

2.2.2 Reduction of Calcined Siderite

Approximately 21 g of the pulverised calcined siderite ore was mixed with 8.4 g pulverised heat-

treated PWS and 0.6 g flour as binder. The mixture was thoroughly mixed and rolled into spherical pellets with dropwise water addition. The pellets were allowed to cure for 72 hours, after which they were allowed to air-dry for a further 72 hours. Each pellet was weighed and then emptied into a fireclay crucible followed by microwave irradiation for 40 minutes. The reduced mass was quickly withdrawn from the oven and its temperature determined using a K-type thermocouple. It was then allowed to cool sufficiently and samples were submitted for XRD and SEM/EDX analyses.

3 Results and Discussion

3.1 Results of Calcination of Siderite Ore

Fig. 2 illustrates the mass loss of the ore and the temperature profile as functions of time. It can be seen from Fig. 2 that the heating rate was constant at about $0.34\text{ }^{\circ}\text{C s}^{-1}$.

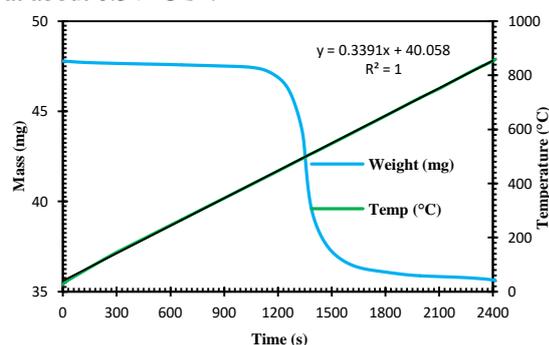


Fig. 2 Thermal Decomposition of Guangzhou Siderite Ore

Calcination of Guangzhou siderite ore became very active from about 1000 s to 1475 s, within which period the mass of the pellet dropped from 47.5 mg to 37.5 mg. The temperature range corresponding to this weight loss was 380 °C to 540 °C. The composition (by XRF) of the calcined ore is shown in Table 2. The Fe_2O_3 content shows a substantial increase from 51.432 wt% (raw ore, Table 1) to 95.852 wt% (calcined ore), corresponding to over 86% increase. The calcined ore was characterised by SEM, SEM/EDS and XRD analyses (Fig. 3-8). The calcined ore shows an irregularly shaped morphology (Fig. 3).

Table 2 XRF of Calcined Siderite Ore.

Component	SiO_2	Al_2O_3	MgO	Na_2O	ZnO
wt %	2.947	0.254	0.220	0.277	0.527
Component	CaO	Fe_2O_3	CuO	Other oxides*	LOI
wt %	0.316	95.852	0.626	0.255	0.401

*Other oxides: K_2O , P_2O_5 , TiO_2 , ZrO_2 , Cr_2O_3 , Mn_3O_4

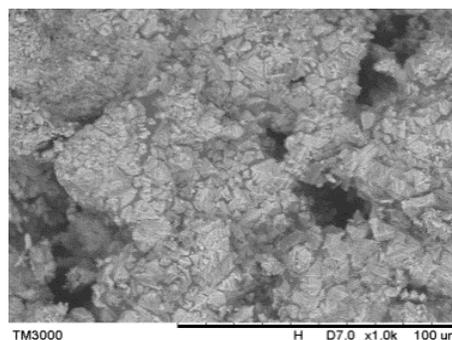
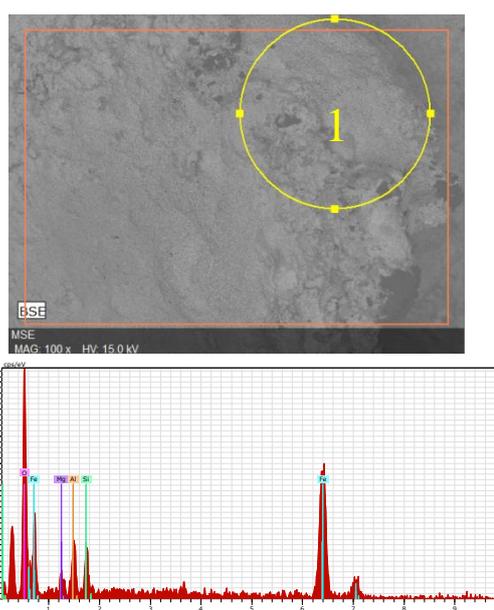


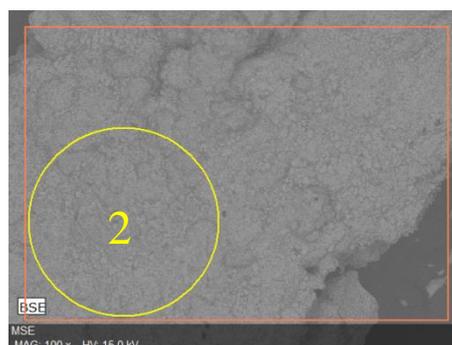
Fig. 3 SEM Micrograph of Solid Product obtained after Calcining Siderite Ore

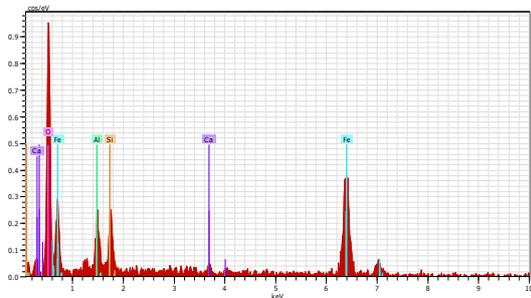
A back scattered electron images of the calcined ore in two regions 1 and 2 are shown in Figs 4 and 5, respectively.



Element (K-series)	Weight %	Atomic %
Fe	63.66	35.41
O	28.79	55.90
Al	3.46	3.98
Si	2.96	3.28
Mg	1.12	1.44
SUM	100	100

Fig. 4 SEM Back Scattered Electron Micrograph of Region 1





Element (K-series)	Weight %	Atomic %
Fe	53.04	26.15
O	37.68	64.85
Si	4.31	4.23
Al	4.09	4.17
Ca	0.88	0.61
SUM	100	100

Fig. 5 SEM Back Scattered Electron Micrograph of Region 2

The content of iron in Regions 1 and 2 are 63.66 and 53.04, respectively. The XRD diffractogram displayed in Fig. 6 shows that the ore was originally composed of $FeCO_3$, which decomposed to maghemite ($\gamma-Fe_2O_3$) after calcination. There appears to be no difference in the diffractograms in Figs 7 and 8, suggesting that HDPE does not have any effect on the final product obtained after calcination.

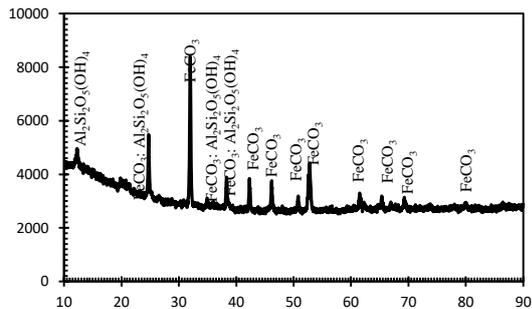


Fig. 6 X-Ray Diffractogram (XRD) of Guangzhou Siderite Ore utilised for the Investigation

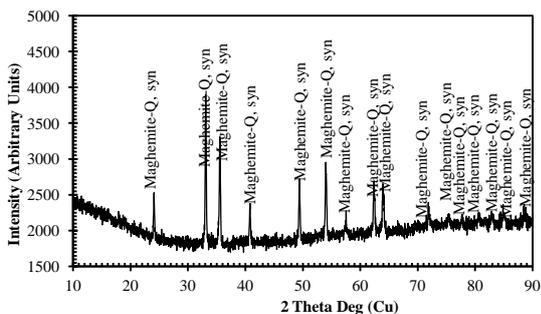


Fig. 7 XRD Diffractogram of Solid Product obtained after Calcining Siderite Ore in Air

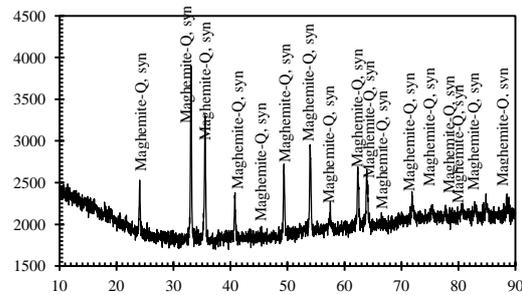


Fig. 8 XRD Diffractogram of Solid Product obtained after Calcining Siderite Ore + HDPE in Air

3.2 Gas Measurement during Calcination of Siderite Ore

The gas emission behaviour during calcination is detailed in the contents of CO , CO_2 and CH_4 in the off gas as measured by a continuous infrared gas analyser. Figs 9 and 10 indicate that the off gas from the calcination of Guangzhou siderite ore in the absence of HDPE consists predominantly of CO_2 and CO . From Fig. 9 the ratio of nCO_2/nCO approaches a value of 2.00 during calcination, suggesting that mechanism 2 is the most likely mechanism in the calcination of Guangzhou siderite ore:

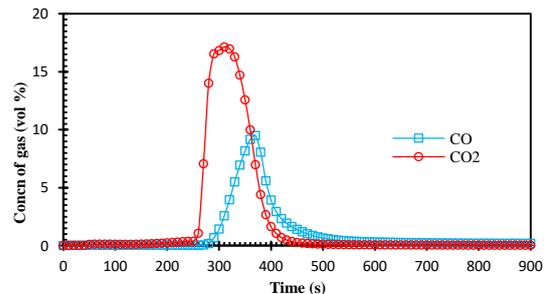
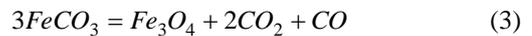


Fig. 9 Gas Emission during Calcination of Siderite Ore in Air

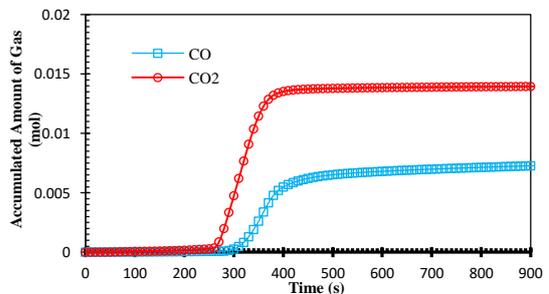
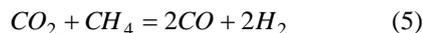


Fig. 10 Gas Generation Behaviour during the Calcination of Siderite Compact

In the presence of HDPE, CH_4 is produced along with the CO and CO_2 , as illustrated in Figs 11 and 12. The presence of HDPE results in a drastic reduction of the accumulated amount CO_2 from 1.396×10^{-2} mol to 7.512×10^{-3} mol after 900 s of

heating. It can be seen that CO becomes the dominant gas as CO₂ declines, suggesting that the CH₄ produced from the thermal decomposition of HDPE is reformed by CO₂ from the calcination of the ore.



From equation (5), the CO₂ generated during calcination of Guangzhou siderite ore can be transformed to syngas, if the ore is mixed with pulverised HDPE. A similar observation was made by Dankwah (2014) in the thermal decomposition of MnCO₃-polymer composite pellets.

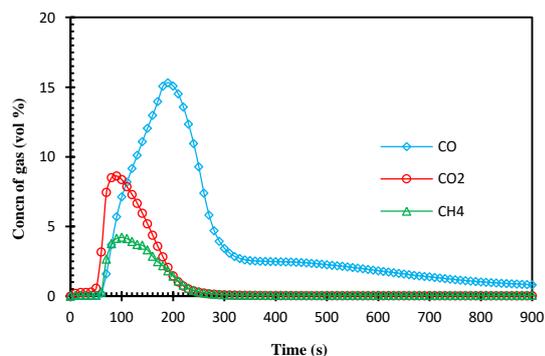


Fig. 11 Gas Emission during Heating of Siderite + HDPE Ore in Air

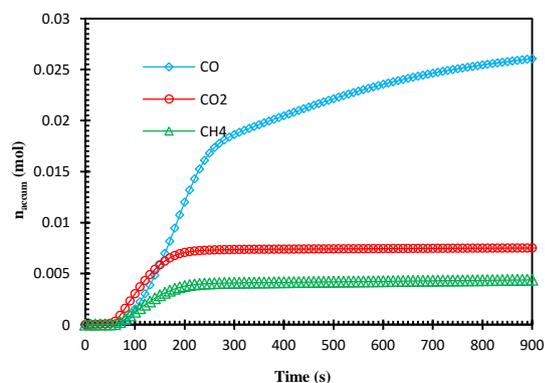


Fig. 12 Gas Emission during Heating of Siderite + HDPE Ore in Air

3.2 Reduction of Calcined Siderite Ore using HDPE as Reductant

Composite pellets of the calcined ore containing measured amounts of HDPE were heated in a horizontal tube furnace in the temperature range 1200 - 1550°C. The XRD diffractogram of the product obtained after 40 mins reduction is shown in Fig. 13. The product consists practically of metallic iron after reduction, evidenced by the sharp peaks displayed in Fig. 13.

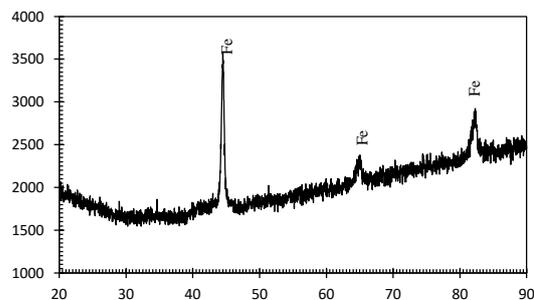


Fig. 13 XRD Diffractogram of Calcined FeCO₃ Reduced with HDPE.

4 Conclusions

The calcination behaviour of Guangzhou siderite ore has been investigated in the presence and absence of HDPE. The calcined product was then reduced with HDPE as reductant. The major findings in this investigation are:

- i. Guangzhou siderite ore (FeCO₃) can be calcined into a high grade magnetic product (γ-Fe₂O₃), that can be reduced by HDPE to produce metallic iron:
- ii. The calcined product is unaffected by the presence of HDPE during the calcination process:
- iii. In the absence of HDPE, the calcination process appears to follow the transformation $3FeCO_3 = Fe_3O_4 + 2CO_2 + CO$, based on the analysis of the exhaust gas.

Acknowledgements

Part of this investigation was conducted at the School of Materials Science and Engineering, University of New South Wales, Australia. The authors are grateful to the various authorising bodies for the permission to carry out the work.

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Authors



Pramod Koshy is currently a Senior Research Fellow at UNSW, Australia. He holds Ph.D. from the School of Materials Science and Engineering, UNSW, Australia. His main areas of research include photocatalytic materials, high-temperature metal/ceramic interfaces, and utilization of waste materials.



James B. Dankwah holds BSc degree in Minerals Engineering at the University of Mines and Technology, Tarkwa, Ghana. He is part of the research group at the University of Mines and Technology currently involved in the recycling of post-consumer plastics in the reduction of metal oxides. His current project is the production of ferrosilicon alloys from the nonmagnetic portion of the Pudo iron ore using end-of-life plastics as reducing agents.



Jessica Dankwah holds BSc degree in Chemical Engineering from the Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. She worked as a Metallurgist at the Damang Mine of Goldfields Ghana Limited as part of her National Service. She is part of the research group at the University of Mines and Technology currently involved in the recycling of post-consumer plastics in the reduction of metal oxides.



James R. Dankwah is an Associate Professor and Head of Minerals Engineering Department at the University of Mines and Technology, UMaT-Tarkwa. He obtained his PhD from the School of Materials Science and Engineering, UNSW-Australia, MSc (Process Metallurgy) from the Norwegian University of Science and Technology and BSc (Metallurgical Engineering) from the Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. His current research areas include iron and steelmaking, high-temperature metallurgical processes, utilisation of waste polymers in metal extraction processes and recycling agricultural waste into building blocks materials for affordable housing for the rural folks. He is a Fellow of the West African Institute of Mining, Metallurgy and Petroleum (WA IMM).