Mineralogical Study of Pingel-Bauchi Malachite Ore

Bamidele Emmanuel, Ajayi John Ade and Elizabeth Makhatha

***Abstract*—Occurrences of over 44 economic minerals has been reported in Nigeria including copper ores found in Bauchi and Zamfara states. Now that the Nigeria petroleum industry which is the mainstay of her economy is experiencing downturn due to the global instability in oil price, it hence become imperative to diversify the economic to solid minerals particularly in the area of value addition. This research work aims at characterizing the Pingel-Bauchi malachite ore in order to determine the mineralogical assemblage, the chemical composition and the micrograph of the minerals. For this purpose, elemental analysis, chemical analysis, ore microscopy, x-ray diffractometry and scanning electron microscopy were carried out on the Pingel-Bauchi malachite ore. The result of the optical and scanning electron microscopy reveal that the Pingel-Bauchi malachite ore occur in a coarse grain locked in a porphyritic fine grain alumina and silica. It was observed that Pingel-Bauchi malachite ore contain 19.8wt% Cu which is above 0 – 2.9wt% Cu which is adjudged to be the minimum copper content for economic extraction of copper ores. It was also observed that the ore contains 3.64wt% iron.**

***Keywords*—** *Malachite, Copper Oxide, Ore, Mineral, Bauchi Copper*

I. Introduction

Nigeria is a highly mineralized nation. Her rich endowment with mineral resources was crucial to her national wealth, strong currency and competitive advantage. Nigeria was a major producer of cassiterite, columbite, coal, clay and limestones till the early 1970. Nigeria was reported the largest producer of columbite at a time and the sixth largest producer of cassiterite at that time. Sixty minerals were estimated to be deposited on the African soil while Nigeria is endowed with forty-four of these sixty [1]. However, with the discovery of crude oil, less attention was paid to the solid mineral sector and the industry has since being in the state of comatose. The effect of the neglect of the solid mineral sector was not that felt until recently when the revenue from the crude oil plummeted after a drastic fall in the selling price of Brent crude [1].

Nigerian geological history is a complex one; which is identified as a Precambrian Basement Complex. It is reported to have evolved from a process of plate tectonic which entails the collision of two blocks – the Pan-African mobile belt and the West African Craton. The Nigerian schist belts are reported to have been deposited in a black-arc basin which was developed after the onset of subduction at the cratonic margin about 600Ma [2].

The occurrence and distribution of copper ore deposit in Nigeria are peculiar to the North. This can be linked to the unique geological structure of the area. The current mining of copper taking place in Nigeria occurs in Nassarawa, Zamfara, Bauchi and Gombe state. However, the explorations of copper in Bauchi state delineate the mineralization of copper to Rishi, Dawa, Kulfana, and Pingel villages. The copper ore obtained in Pingel village of bauchi state is used to carry out this investigation. Typical occurrences in Pingel were reported to consist of disseminated malachite and azurite ores hosted in coarse grained to porphyritic granite.

Previous studies have been carried out on different copper ores using microscopy. [3] used an electron microscope to study the microstructure of copper in his work on the studies of the physiology of microorganisms associated with leaching of copper. Also, [4], [5] ,[6]–[8] all employed the use of optical and electron microscopy in the micron and submicron level investigation of different copper ores or materials having copper and other elements contained in them.

This experiment apply SEM-EDS, this align with the opinion of [9] that scanning electron microscopy reveals texture that cannot be observed by optical microscopy.

Other characterization carried out in this research employed the use of X-ray Fluorescense, Atomic Absorption Spectrometry and X-ray diffractometer in measuring the elemental content contained in the ore and the mineralogical assemblage of the ore. XRF is chosen due to its advantage of ease of sample preparation, stability and ease of use of x-ray spectrometer [10]. Different analysis on copper ore had been carried out by various researchers using the XRF, AAS and XRD on minerals and materials containing copper and iron. Some of these studies are [11], [12], [13], [14], [15], [16] and [17].

The current diversification plan of the Nigerian economy from petroleum products to Agriculture and solid minerals calls for detailed investigations and study of the different minerals whose deposits have been proven in the country; hence, the reason for this study. Our aim is to carry out quantitative and qualitative analysis of malachite ore obtained from the Pingel village in Bauchi state while assessing the results comparably with the occurrence of the ore.

E. A. Bamidele is with the Department of Metallurgy, University of Johannesburg.

John A. Ajayi was with Federal University of Technology Akure Nigeria. He is currently on Sabbatical in the Department of Metallurgical and Materials Engineering, University of Lagos, Nigeria.

E. Makhatha is with the Department of Metallurgy, University of Johannesburg.

II. EXPERIMENTAL

A. Weighing and Sampling

Malachite ore was obtained from the Pingel village of the Toro Local Government area of Bauchi state, Nigeria. Chisel and jackhammers were used to collect samples from the activities of the artisanal miners in the study area. The pits from which samples were collected maintained parallel alignment to the width of the deposit. Malachite ore was collected towards the North East of the deposit. 800g of malachite was weighed using digital weighing balance. Ore sorting was then carried out to expose the malachite from the associated gangues and soil.

B. Chemical Analysis of Pingel-Bauchi Malachite Ore

The elemental analysis of the Pingel-Bauchi malachite ore was carried out using the atomic absorption spectroscope (AAS) of the Central Research Laboratory of the Federal University of Technology, Akure. The result of the elemental analysis is presented in Table I.

Chemical analysis of the malachite ore was carried out using the x-ray fluorescence (XRF) of the Ahmadu Bello University Analytical Laboratory. 20g of the malachite ore was pulverized to the powder form, the powdered ore was thereafter fed into the sample holder of the XRF equipment. The chemical composition of the Pingel-Bauchi malachite ore is shown in Table II.

C. Microscopy and Mineralogical Assemblage of Pingel-Bauchi Malachite Ore

Ore Microscopy - Ore microscopy was carried out on the Pingel-Bauchi malachite ore at the National Metallurgical Development Centre, Jos, Nigeria. 30g of the malachite sample and 30g of the azurite sample were weighed. The samples were cut into blocks which were then mounted using the mounting press with the phenolic powder. The mounted samples were rubbed on the grinding machine using the 120 grade silicon carbide, then on 240, 400, 600 and 1000 grades silicon carbide belt grinder. The samples were then polished and dried before viewing on the optical microscope which was equipped with high resolution digital camera for both transmitted and reflected light. The photomicrograph of the mounted malachite samples are shown in Plate 1a and 1b.

X-ray Diffractometry -Determination of the mineral assemblage of the malachite ore was carried out using the X-ray Diffractometer (XRD) at the Defence Industries Corporation of Nigeria (DICON), Kaduna, Nigeria. 20g of the sample was pulverized and illuminated with x-rays of fixed wavelength. The x-rays were reflected and radiated. The intensity of the reflected radiation was then recorded. The resulting diffractogram is shown in Fig. 1.

D. Scanning Electron Microscopy

Mineralogical characterization of the malachite ore showing two dimensional image which reveals texture and crystalline structure was carried out using scanning electron microscope (SEM) of the Instrumentation laboratory of the Chemical Engineering Department of Ahmadu Bello University, Zaria, Nigeria. SEM with one detector (secondary electron detector) was used. 5g of malachite ore sample was placed in SEM chamber and a beam of high energy electron was focused from the electron lenses towards the SEM chamber to generate a variety of signal at the surface of the 5g malachite sample. The signals generated from the electron and sample interactions generate a two dimensional image revealing the texture and crystalline structures of the malachite at magnifications of 500X, 1000X, 1500X and 3000X. The micrographs obtained are shown in Plate 2a, 2b, 2c and 2d.

III. RESULTS AND DISCUSSION

Chemical Analysis of Pingel-Bauchi Malachite Ore

The result of the elemental analysis carried out on the Pingel-Bauchi malachite ore sample is presented in Table I.

TABLE I: ELEMENTAL ANALYSIS OF THE PINGEL-BAUCHI MALACHITE ORE USING AAS

Sample	Cd (ppm)	Cu (ppm)	Pb (ppm)	Fe (ppm)	Mn (ppm)	Na (ppm)
Malachite	38.00	195 200.00	248.00	36400.00	114.00	4.60

In addition, the result of the chemical analysis carried out on the Pingel-Bauchi Malachite Ore using XRF is shown in Table II.

TABLE II: CHEMICAL COMPOSITION OF BAUCHI MALACHITE ORE USING THE XRF

S/N	Oxide of Elements Present	Composition (%wt)
1.	Na_2O	2.626
2.	MgO	0.778
3.	Al_2O_3	19.176
4.	SiO_2	22.274
5.	P_2O_5	1.170
6.	K_2O	1.083
7.	CaO	0.437
8.	TiO_2	0.616
9.	Fe_2O_3	5.524
10.	CuO	19.562

The elemental analysis carried out on the Pingel-Bauchi malachite ore as shown in Table I reveals that the ore contains 19.5wt%Cu, 3.64wt%Fe, 1.10wt%Mn, 2.48wt%Pb, 0.40wt% Cd and 0.5wt%Na. The result shows that the Pingel-Bauchi malachite ore has appreciable copper content. The 19.5wt% obtained is above the 0 – 2.9wt% which [15] prescribed for an economically worthwhile extraction. However, the result obtained from the use of XRF shows a similar weight percentage of copper in the malachite ore.

The principal element present in the copper ore is iron which is shown in Table I and Table II. From the result of the analysis, 3.64wt% Fe was revealed in the Pingel-Bauchi malachite ore. This weight percent of iron in the Pingel-Bauchi malachite ore conforms to the assertion of [18] that the iron content of typical copper oxide ore is between 2% and 6%. This also tallies with the observation of [19] that in most oxide copper ore deposits including malachite, iron is present in a variety of oxide, hydroxide, sulfate, sulfide and silicate minerals. In this case,

iron is present in its oxide state. The 3.64wt% of iron contained in the ore satisfy the requirement for proper leaching of the ore, this is due to the iron content staying between the 2% and 6% prescribed for moderate reaction of malachite with the acidic lixiviants Nordstorm and Aspers (1998).

A. Microscopy and Mineralogical Assemblage of Pingel-Bauchi Malachite Ore

Ore Microscopy - The result obtained from the ore microscopy carried out on the malachite ore is displayed in Plate 1 and 2. The photo micrograph shows coarse malachite, locked within fine grained silica in association with alumina. Hematite can also be observed at the boundary of the malachite grains.

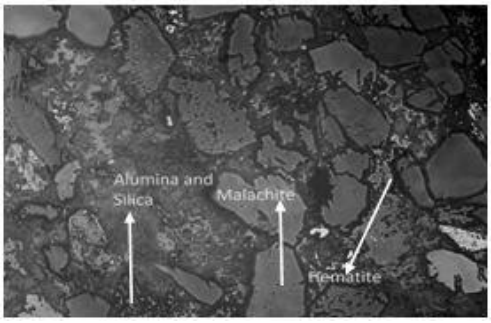

Plate 1a: Photo-micrograph of Pingel-Bauchi Malachite Ore

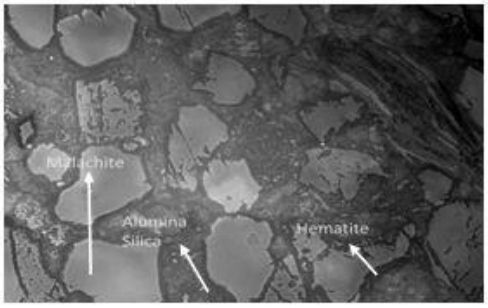

Plate 1b: Photo-micrograph of Pingel-Bauchi Malachite Ore

Plates 1a and 1b show the microstructure of Pingel-Bauchi malachite ore. It depicts the occurrence of coarse grained malachite which is locked within the porphyritic fine grains of alumina which is associated with silica. The hematite seen among the composition of the malachite ore in Plates 1a and 1b conforms with the fact made by [6]that hematite is found in association with the malachite in a criss-cross cut fashion across the cleavages and grain boundaries of the malachite.. [6] and [19] argued that the occurrence of carbonate minerals – including malachite and azurite ores - at the surface of the deposit shows the occurrence of secondary copper minerals deep in the earth crust among which we have chalcopyrite. Plates 1a and 1b suggest a deep occurrence of sulphide minerals at or around the deposit in conformity to [20] assertions that malachite occurrence is due to the weathering of the sulphide deposits under the climatic conditions prevalent at the site of mineralization.

B. X-ray Diffraction

The minerals associated with the malachite ore in the sample obtained from the deposit is shown in Fig. 1.

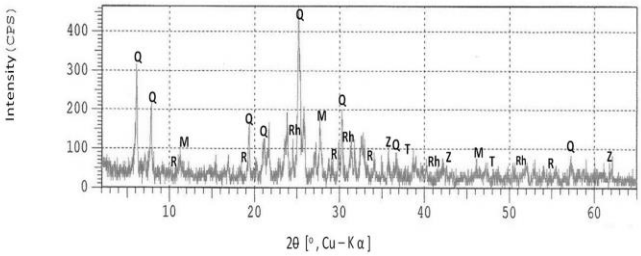

Fig 1: X-ray Diffractograph of the Malachite Ore [Q: Quartz; R: Riebeckite; M: Malachite; Rh: Rhodochrosite; Z: Zincite; T: Tenorite;]

As shown by the diffractogram of Bauchi malachite ore, the traces of iron and manganese in some of the minerals/compounds like; hematite, riebekit, rhodocrosite and magnesium iron aluminium silicate hydroxide; shows that the Bauchi malachite ore is formed by weathering of primary copper deposits as deduced by [19].

Scanning Electron Microscopy

The results of the scanning electron microscopy of the Pingel-Bauchi malachite ore determined are shown in Plates 2a and 2b.

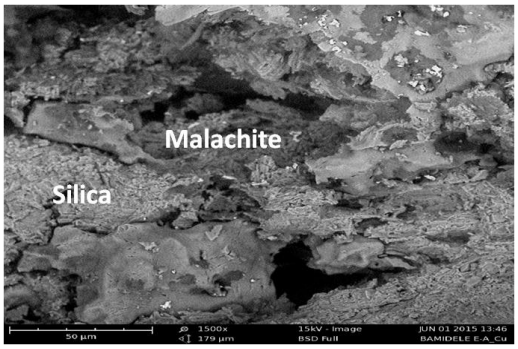

Plate 2a: Scanning Electron Micrograph of the Bauchi malachite ore at 1500X magnification and 50*u*m spatial resolution.

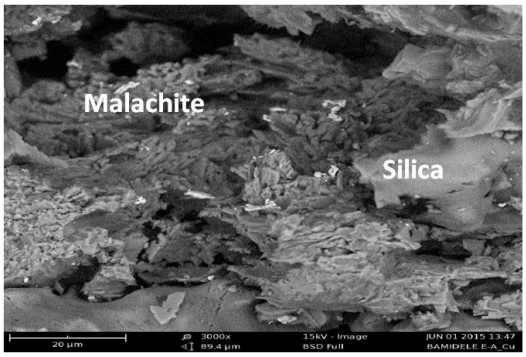

Plate 2b: Scanning Electron Micrograph of the Bauchi malachite ore at 3000X magnification and 20*u*m spatial resolution.

The micrograph obtained from the scanning electron microscopy shown in Plates 2a and 2b shows the surface topography of the Bauchi malachite ore. It shows a fibrous

malachite texture with an acicular hematite running around the boundary. Another phase on the morphology revealed by the secondary electron detectors shows the fine silica associated with the alumina in association within it.

The micrograph conforms to that of Katanga copper deposit (Zambia) which was studied by [21]; the malachite occurs as fibrous malachite with other minerals; and also the opinion of [2] that the fibrous malachite occurs in association with quartz in fine surface as depicted in Plates 2a, and 2b.

CONCLUSION

This research encompasses the sampling of the Pingel-Bauchi malachite ore, chemical analysis and mineralogical analysis -including x-ray diffractometry and scanning electron microscopy. The findings from the research are:

1. Pingel-Bauchi malachite ore contains 19.5% concentration of copper after ore sorting which is higher than the established 0 – 2.9 % concentration.
2. Pingel-Bauchi malachite ore contains 3.64% concentration iron which falls within the 2 – 6% concentration required in copper oxide ores.
3. Pingel-Bauchi malachite is locked in a locked within the porphyritic fine grains of alumina which is associated with silica.
4. Malachite ore (Copper oxide ores) can be formed by the weathering of complex sulphide copper minerals.
5. Pingel-Bauchi malachite ore deposit indicates a deeper occurrence of copper mineral due to its nature obtained from mineralogical examination.

ACKNOWLEDGMENT

The authors of this publication wishes to acknowledge the contributions of the management of Nigerian Institute of Mining and Geosciences for facilitating the procurement of the ore; and Dr. Ayeni Afolabi of the University of Saskatchewan, Canada for his role in facilitating the testing.

REFERENCES

[1] [O. S. Ayodele, S. Akongwale, and U. P. Nnadozie, "Economic Diversification in Nigeria: Any Role for Solid Mineral Development?," *Mediterr. J. Soc. Sci.*, vol. 4, no. 6, p. 691, 2013.

[2] Anon, "Copper Exploration Opportunities in Nigeria," Abuja, 2014.

[3] K. M. Paknikar, "Studies on physiology of microorganisms associated with leaching of copper." 2017.

[4] Y.-J. Hsu, Z. Zajacz, P. Ulmer, and C. A. Heinrich, "Copper partitioning between silicate melts and amphibole: Experimental insight into magma evolution leading to porphyry copper ore formation," *Chem. Geol.*, vol. 448, pp. 151–163, 2017. https://doi.org/10.1016/j.chemgeo.2016.11.019

[5] A. A. Baba, M. K. Ghosh, S. R. Pradhan, D. S. Rao, A. Baral, and F. A. Adekola, "Characterization and kinetic study on ammonia leaching of complex copper ore," *Trans. Nonferrous Met. Soc. China*, vol. 24, no. 5, pp. 1587–1595, 2014. https://doi.org/10.1016/S1003-6326(14)63229-5

[6] S. Panda *et al.*, "Extraction of copper from copper slag: Mineralogical insights, physical beneficiation and bioleaching studies," *Korean J. Chem. Eng.*, vol. 32, no. 4, pp. 667–676, 2015. https://doi.org/10.1007/s11814-014-0298-6

[7] C. L. Ciobanu, N. J. Cook, and K. Ehrig, "Ore minerals down to the nanoscale: Cu-(Fe)-sulphides from the iron oxide copper gold deposit at Olympic Dam, South Australia," *Ore Geol. Rev.*, vol. 81, pp. 1218–1235, 2017. https://doi.org/10.1016/j.oregeorev.2016.08.015

[8] H. M. Jassim, H. Z. A. Toma, and L. S. Oudah, "Solvent Extraction and Electro-Wining from Copper Leaching Product of Mawat Sulfide Ore Using Taguchi Method," *UKH J. Sci. Eng.*, vol. 1, no. 1, pp. 53–59, 2017. https://doi.org/10.25079/ukhjse.v1n1y2017.pp53-59

[9] B. Rusk and M. Reed, "Scanning electron microscope–cathodoluminescence analysis of quartz reveals complex growth histories in veins from the Butte porphyry copper deposit, Montana," *Geology*, vol. 30, no. 8, pp. 727–730, 2002. https://doi.org/10.1130/0091-7613(2002)030<0727:SEMCAO>2.0.CO;2

[10] A. Dehghan, K. Peterson, G. Riehm, and L. H. Bromerchenkel, "Application of X-ray microfluorescence for the determination of chloride diffusion coefficients in concrete chloride penetration experiments," *Constr. Build. Mater.*, vol. 148, pp. 85–95, 2017. https://doi.org/10.1016/j.conbuildmat.2017.05.072

[11] T. E. La Tour, "Analysis of rocks using X-ray fluorescence spectrometry," *Rigaku J.*, vol. 6, no. 1, pp. 3–9, 1989.

[12] G. Budak and A. Karabulut, "X-ray fluorescence analysis of malachite ore concentrates in the Narman region," *Spectrochim. Acta Part B At. Spectrosc.*, vol. 54, no. 6, pp. 985–988, 1999.

[13] K. Castro, A. Sarmiento, I. Martínez-Arkarazo, J. M. Madariaga, and L. A. Fernández, "Green copper pigments biodegradation in cultural heritage: from malachite to moolooite, thermodynamic modeling, X-ray fluorescence, and Raman evidence," *Anal. Chem.*, vol. 80, no. 11, pp. 4103–4110, 2008.

[14] Y.-Z. Zhang, B. Zhou, X.-P. Zhang, P. Huang, C.-H. Li, and Y. Liu, "Interaction of malachite green with bovine serum albumin: determination of the binding mechanism and binding site by spectroscopic methods," *J. Hazard. Mater.*, vol. 163, no. 2–3, pp. 1345–1352, 2009. https://doi.org/10.1016/j.jhazmat.2008.07.132

[15] P. Escarate, R. Hein, M. Duran, and P. Ramaciotti, "X-ray fluorescence spectroscopy for accurate copper estimation," *Miner. Eng.*, vol. 71, pp. 13–15, 2015. https://doi.org/10.1016/j.mineng.2014.10.016

[16] R. L. Frost, Z. Ding, J. T. Kloprogge, and W. N. Martens, "Thermal stability of azurite and malachite in relation to the formation of mediaeval glass and glazes," *Thermochim. Acta*, vol. 390, no. 1–2, pp. 133–144, 2002. https://doi.org/10.1016/S0040-6031(02)00127-2

[17] S.-H. Huo and X.-P. Yan, "Metal–organic framework MIL-100 (Fe) for the adsorption of malachite green from aqueous solution," *J. Mater. Chem.*, vol. 22, no. 15, pp. 7449–7455, 2012. https://doi.org/10.1039/c2jm16513a

[18] C. N. Alpers and D. K. Nordstrom, "Geochemical modeling of water-rock interactions in mining environments," *Rev. Econ. Geol.*, vol. 6, pp. 289–324, 1999.

[19] J. E. Dreier, "The chemistry of copper heap leaching," *Source< http//jedreiergeo. com/copper/article1/Chemistry_of_Copper_Leaching. html*, 1999.

[20] S. Van Langendonck, P. Muchez, S. Dewaele, A. K. Kalubi, and J. Cailteux, "Petrographic and mineralogical study of the sediment-hosted Cu-Co ore deposit at Kambove West in the central part of the Katanga Copperbelt (DRC)," *Geol. Belgica*, 2013.

[21] F. Mees, T. De Putter, S. Decrée, and S. Dewaele, "Petrographical features of malachite from Katanga as indicators of mineral formation processes–preliminary results," *Le Sect. Min. la République démocratique du Congo à la croisée des chemins. R. Museum Cent. Africa, Tervuren*, pp. 73–74, 2012.

Emmanuel A. Bamidele is a graduate student in the department of engineering and extraction metallurgy, University of Johannesburg. He obtained a Bachelor of Engineering (Hons) degree in metallurgical and materials engineering, from the Federal University of Technology, Akure in 2015.

He worked as a Mineral Processing Engineer II in Santago Nigeria Limited in 2016 before proceeding to Elipse International Ex Solution Limited as a Geometallurgist. He became a Member of the Nigerian Institute of Metallurgical, Mining and Materials Engineers Society (a division of the Nigerian Society of Engineers) in 2017. He is also a member of the Nigerian Metallurgical Society.

Mr. Bamidele was awarded the Global Excellence Stature Scholarship in November 2017 to undertake Masters Degree program in Metallurgy at the University of Johannesburg. He has six publications and two research papers currently under review. His current area of interest revolves round solving some pressing environmental issues in the extractive metallurgical industry especially the application of selective chemical separation.