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Keywords

chalcopyrite, characterisation, liberation, flotation grade, recovery

Exploring the Characterization, Liberation and Flotation Response of a Nigerian Low-Grade Copper Ore

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Abstract

This study explores the characterization, liberation and flotation response of low-grade copper ore from Anka area, Zamfara state Nigeria. The ore was crushed, milled and sieved in accordance with BS 410 standard. It was characterized with XRD, XRF, SEM-EDS and AAS. Froth flotation was carried out with varying % solids, pH, retention time and collector dosages using SEX and sodium oleate. Particle size distribution of the ore shows its economic liberation between −150 and +106 μm while 80% passing corresponds to 175.7 μm using the Gaudin Schuhmann equation. However, according to metallurgical balance calculation, 63 μm proved to have the highest metal content. Identified peaks of the copper ore by XRD revealed the presence of pyrite and chalcopyrite as the major mineral content at 47 and 36%, respectively, while other elements were present in traces. XRF shows Fe and Cu as the major elements and others in traces. Morphology, according to SEM-EDS, revealed that Fe is the major impurity while the presence of Cu and S confirmed chalcopyrite is present in the ore minerals. AAS shows an average of 25.87% Cu and 32% Fe in the ore. Optimum recoveries of copper were recorded at 30% solids, pH of 8, 30 min retention time. The highest recovery of 95.94% was recorded with SEX at 0.25 mol/dm^3, while recoveries were lower with PAX, the highest recovery being 33% at 0.20 mol/dm^3 0.25 mol/dm^3 of SEX recorded the highest yield and enrichment ratio of 40.38 and 2.38, respectively.

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1. Introduction

Copper has been said to be one of the first metals used by man. It is a very important metal utilised for several purposes in many sectors. It has been utilised for producing electric cables, water pipes, pins and plugs, coins and several other appliances. This makes it to be on demand every day. It was reported by the copper industry of Africa that the highest consumption of copper is in Asia Oceania [1]. Americans have dominated the world market because of the demand in the manufacturing industry. However, it is expected very soon that there could be fluctuation in the world market caused by transportation issues, cost of infrastructures and several requirements, policies or legal norms for mining activities. In Africa, many countries have contributed to the production of copper, and the trail has been led by Uganda, Zambia, South Africa and Katanga province of the Democratic Republic of Congo. Meanwhile, there is a high copper deposit in Baluba, East of Luska Zambia [2,3].

It has been reported that copper is one of the important non-ferrous metals having so many areas of commercial applications. Copper is used in the electrical industries mostly because of its high ductility and high electrical conductivity, thereby causing high demand for the metal [4]. Other uses of copper include the production of a variety of facilities, accessories, or parts for medical and health care systems, pipes and tubes, automobile radiators,

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household items and kitchen wares. It also forms part of the production component of metal alloys like brass (copper + zinc) and bronze (Cu + Sn). Copper is used as a pigment in painting, a preservative for textile materials, wood and paper. Many of these items also have their uses in the various industrial sectors.

Most base metals are derived from sulfide ores, and copper is one of these metals. Others are lead, zinc, iron, cobalt and molybdenum. It has been reported that copper is the most important non-ferrous metal, which has so many areas of commercial applications [5–9]. Examples of copper sulfide minerals are pyrite (FeS_2), covellite (CuS), chalcocite (Cu_2S) and chalcopyrite. It has been observed that if the main copper mineral of sulphide ore is chalcopyrite ($CuFeS_2$), then it can be easily processed. However, if it contains other minerals like chalcocite and covellite, it may not be easy to depress the pyrite inside.

Froth flotation has been a highly useful method of processing sulphide minerals because it has been ascertained over the years that the method is effective [10]. The complexity in the mineralogical composition of most sulphide minerals has necessitated the selectivity in their processing. They are sometimes composed of minerals which can rarely be differentiated from one another due to the closeness in their mineralogy. Sometimes the deposits are possibly composed of oxides, carbonates, silicates or mixed ores [11]. Processing minerals of such nature without understanding mineralogy can be a waste of time. Understanding mineralogical composition of any deposits enhances effective processing because it will assist in choosing the best mineral processing route(s). Characterization of ore deposits before comminution is therefore very germane because it involves quantitative and qualitative analysis.

Oyelola et al. [12], Davenport [13], and T & Bosan ascertained that froth flotation is a very versatile method of concentrating minerals because it has given room for mining deposits which could have ordinarily been regarded as uneconomical because of a low grade and complexity in mineralogical compositions of the ore bodies. Apart from mineralogy, the next factor to consider when to float minerals is their ability or inability to get wetted or to adhere to air in the cause of separation. Most of the solid minerals are hydrophilic; therefore, one portion must be rendered aerophobic while the other is rendered hydrophobic. This is achieved by engaging chemicals or reagents most important of which is the collector. Other reagents are pH modifiers, depressants, frothers and activators. Each of these reagents has its different functions in enhancing the recovery of valuable minerals from the ores.

Copper occurs as sulphide, carbonates or oxide minerals. However, it was discovered that the conventional method of processing, like pyrometallurgy, has not been adequate to yield the highest quality copper metal unlike when one or two other methods are employed especially the hydrometallurgical processes [15]. To effectively produce copper from its crude ores, some steps are usually followed in treating the ores. Firstly, the crude copper can be pre-concentrated by froth flotation, in which case the run of mine is crushed, milled, screened and treated with reagents and chemicals to obtain the valuable portion of the ore from the gangue [12]. An alternative to this partial roasting is to obtain calcines or oxidized materials. Secondly, the copper concentrate (which has improved grade) is passed through a two-stage pyrometallurgical extraction by smelting the concentrate to matte and converting the matte to copper (crude copper). Finally, the crude copper is refined by firing to produce the refined copper and lastly, the high purity electrolytic copper through the electro refining process. Fig. 1 shows the general production process according to [15]. Flotation had been a gainful method of concentrating copper ore owing to the fact that 80% of primary copper production comes from low-grade ores [15,16].

The flotation of copper minerals has been investigated by several authors; Flotation of copper sulphide requires sulfhydryl or thiol types of collectors generally consisting of the SH group in combination with an organic radical, which is said to have extensive application. Bulatovic [17,18] investigated the micro flotation of chalcopyrite and pyrite minerals mixture using sodium ethyl xanthate, SEX and antihate chalcopyrite and pyrite were floated with SEX to establish a baseline reference for the comparison with floatability of the mixed minerals. The collector dosage was approximately 50%. The results show that recoveries without the collector are 10.8% pyrite and 65.4% chalcopyrite. However, with the addition of the collector (SEX), the recoveries were 83.8% and 85.5% of pyrite and chalcopyrite, respectively. When the same process was repeated with diethyl-DTC, recoveries were up to 91.7% and 93.4% of pyrite and chalcopyrite, respectively [15]. The thermochemical behaviour of thiol collectors and collector mixtures with sulphide minerals was studied by Abdulfattah F et al. [19]. The flotation kinetics and thermodynamics behaviour of chalcopyrite and pyrite in high alkaline systems were investigated by Yan H et al. [5]. Monomineral

Fig. 1. General copper production process according to Davenport [13].

flotation and microcalorimetry were used to study the flotation kinetics and thermodynamics behaviour of both minerals in lime and sodium hydroxide. The results show that there were fewer hydrophilic substances on the chalcopyrite, which caused the apparent activation energy of sodium butyl xanthate, and SBX absorption in chalcopyrite to be low. In other words: the absorption of SBX was enhanced, thereby increasing the floatation rate and recovery of chalcopyrite. On the other hand, the absorption of activation energy of SBX was high on the pyrite surface, which hindered high pyrite recovery. Potassium ethyl xanthate has been reported to have enhanced hydrophobicity and promotion of bubbles in the flotation of low-grade copper ore [10,22]. It has been reported that the total loss of copper-bearing minerals in 0.020−0.071 mm size fraction of tailings production from Lubin Concentrator Plant (KGHM Polska Miedz SA Group) was found to be 52% [17]. This loss was attributed to complexity in mineralogical characteristics.

In Nigeria, copper is one of the numerous minerals that the country has been endowed with. It is found in many areas, including Zamfara state, where this study was carried out. Some authors have carried out research on copper mineral deposits in Nigeria. The characterization of Nigerian copper ore deposit had been studied by several authors [22,23] and it was reported that the copper ore contains 18.07% Fe, 3.30% Cu, 0.78% Pb, 0.48% Mn, 1.43% Ca, 0.66% Sn, 0.03% Sr, 0.11% Zn, 0.03% Zr, 0.34% Ti, 0.02% Nb, 0.03% Sb, 0.03% Ag, 0.07% As, 19.62% Si and 1.66% S. Usaini et al. worked on the determination of liberation size of Akiri Copper Ore [20]. Chemical and sieve analyses of the sample were carried out, and it was established that both economic and actual liberation size is 125 μm. The determination of chemical composition and work index of Rafin Gabas chalcopyrite ore had been studied by Oyeladun et al. [21], and the copper content of the ore was reported to be 12.6%. Meanwhile, it was also reported that the work index of the same deposit was found to be 22.38 kWh/tonne.

The focus of this present study is to investigate the characterization, liberation characteristics and flotation response of Zamfara low-grade copper ore. The study includes sourcing the copper ore sample, preparing the sample for detailed analysis via particle size analysis, chemical composition, mineralogical examination and froth flotation of the minerals.

2. Experimental

2.1. Sample sourcing and preparation

The copper ore for this work was sourced from Zamfara State, Nigeria, located on 12° 06″30′N and 5°56″ 00′E. 5 kg of the sample was crushed to reduce the boulders to about 4″ using a Denver jaw crusher (primary). After that, the product was further crushed to reduce the sizes to 1″, which was the minimum set of the *Fritsch pulverisette* (No 013 type 1060) engaged in the further crushing process. A Denver laboratory ball mill was involved in milling the sample using 10 big steel balls of size 45 g each and 4.2 cm diameter, and smaller balls of 15 g each and 10 mm in diameter. The combination of the two sizes was engaged to ensure proper milling within a stipulated time of 20 min. The product was after that collected and taken to the sieving section.

2.2. Particle size analysis

A set of Endecott BS 410 comprises six sieves selected by using root two series to select successive sieves used for the sieving. The set was arranged in descending order of aperture and was placed on the base span. 300 g of the test sample was weighed and placed on the uppermost sieve, which was later covered with the sieve led to avoid a loss of the sample during shaking. The sieve shaker that was used for this purpose was Pascal's engineering sieve shaker model, and the set of sieves selected were 300, 212, 150, 106, 75, and 63 μm. After sieving for 5 min, the sieves were carefully separated to collect the retained particles on each sieve, and the results were recorded and statistically analysed.

2.3. Determination of X-ray diffraction pattern of Zamfara copper ore

Samples were prepared using a back loading system. After cleaning the sample holder and the back piece with acetone and filling the ring with enough sample in the ring just above the cup level, the sample was loaded. The test was then carried out using a PANanalytical X'pert pro diffractometer with X′ elevator and variable divergence and receiving slits each set at 10 mm with Nb filtered Co α k radiation. The sample was scanned at angle 2θ, and the relative phase amounts (weights %) were estimated using the Rietveld method. X'pert high score plus software was used for the analysis of the results.

2.4. Quantitative analysis of the major elements within the chalcopyrite ore

X-Ray Fluorescence, XRF analysis was carried out using the XRF- ZSX Primus II to determine the composition of the ore. 2 g each of the sample were added to 1 g of Sasol wax binder, which was milled and mixed thoroughly together in a laboratory

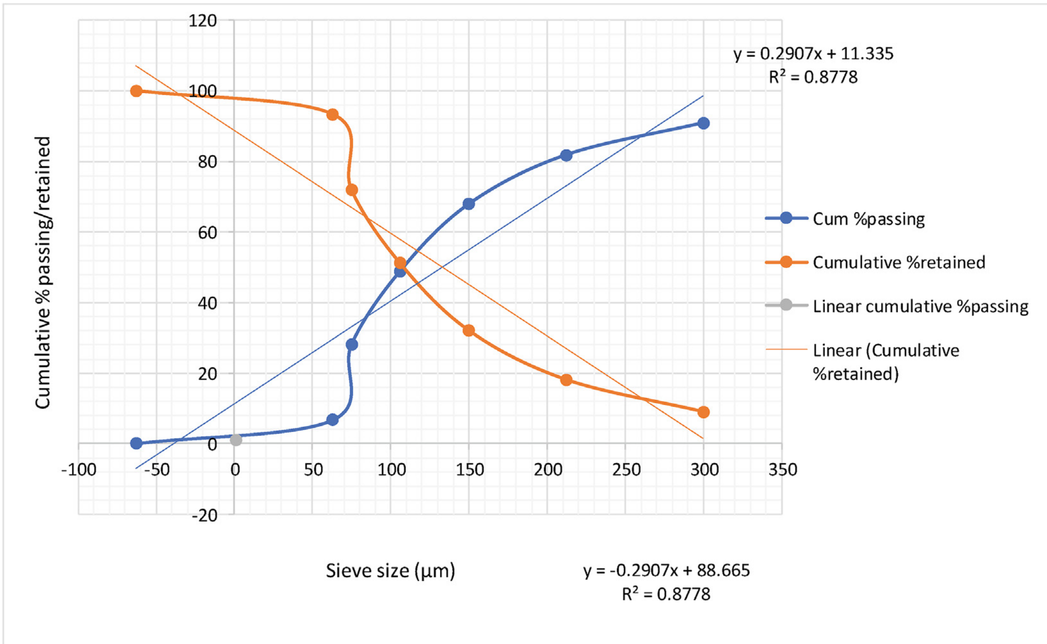


Fig. 2. *The plot of sieve analysis.*

mortar and pestle to form a homogenous mixture. The resulting product was poured into the aluminium cup, hydraulically pressed to form pellets, and the pellets were subsequently kept in the oven at 50 °C.

2.5. *The surface morphology of chalcopyrite ore*

Scanned Emission Microscopy/Energy Dispersed Spectrometry (SEM-EDS) was carried out with (SEM-EDS) TESCAN VEGA 3 LMH and a spatter coating machine (QUORUM 150T E). The machine was run with a voltage of 20 kV and a working distance of 15 mm between the specimen and the detector. The software engaged was Oxford software to determine the morphology of the sample via the grain size, shape, structure, and degree of association of major, minor, trace elements and compounds in the ore.

2.6. *Determination of the elemental composition of the Nigerian chalcopyrite ore by AAS*

The chemical compositions of the samples were determined using an atomic absorption spectro

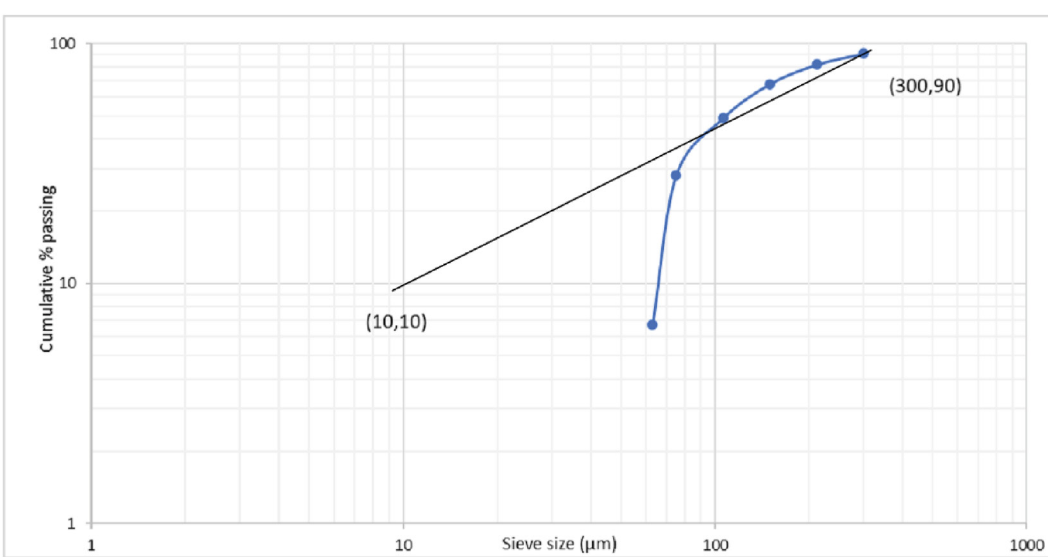


Fig. 3. *Gaudin Schuhmann plot of PSD of the Nigerian chalcopyrite ore.*

Table 1. Size distribution versus liberation and percentage distribution of the metal content in the chalcopyrite ore.

Sieve range (μm)	Nominal aperture (μm)	Retained weight (g)	Weight retained %	Cum passing %	Cumulative retained %	Assay of Cu	Metal content	Distribution %
300	300	27.12	9.04	90.96	9.04	11.17	302.95	8.34
300 + 212	212	27.46	9.15	81.81	18.19	11.53	316.60	8.72
212 + 150	150	41.61	13.87	67.94	32.06	11.83	492.07	13.55
150 + 106	106	57.2	19.07	48.87	51.13	11.91	681.49	18.77
106 + 75	75	62.24	20.75	28.12	71.88	12.16	756.93	20.84
75 + 63	63	64.24	21.41	6.71	93.29	12.82	823.43	22.67
+75-63	−63	20.13	6.71	0.00	100.00	12.82	258.03	7.11
							3631.503	

meter (AAS). The method of extraction used to digest the sample was the Aqua regia extraction method. The pebbles of the samples were pulverised using the pot pulveriser, and 2 g of each of the samples were added to 28 ml of aqua regia (HCl: HNO_3 in ratio 3:1). The suspension was digested at ambient temperature for 16 h and later digested at 1300 °C for 2 h. The obtained suspension was then filtered through ashless Whatman 41 filter paper, diluted with distilled water up to 100 ml and stored in plastic sample bottles. The resulting solution was analysed using the AAS.

2.7. Flotation study of the Nigerian chalcopyrite ore

Froth flotation tests were conducted on the chalcopyrite ore using the Denver D-12 flotation cell rotated at a speed of 1300 r/min. 15% solids of the pulp was prepared in a 250 g tank. 5 g of soluble corn starch was added to depress Fe content in the pulp. SEX was added to the pulp at 0.15 mol/dm^3, while 1 ml pine oil was added as the frother at a pH of 8, which was obtained by adding NaOH. The experiment was repeated for 30 and 45% solids. The recovered concentrate weights for the 15, 30 and 45% were compared. 30% solids gave the highest weight concentrate. Therefore, the froth flotation test was repeated, keeping a solid level at 30% and varying pH. Sulphuric acid was added to lower the pH of the pulp while all other parameters were kept constant. The test was repeated for pH 6 and 10. Thereafter, the test was repeated for 15, 30 and 45 min retention time. All the concentrates were statistically analysed. The optimum parameters were later used to compare the effectiveness of sodium oleate to sodium ethyl xanthate.

3. Results and discussion

3.1. Particle size distribution of the Nigerian chalcopyrite ore

Fig. 2 shows the particle size distribution of the Nigerian chalcopyrite ore. D_{50} is equal to −150 + 106 μm, the same point at which the curves of cumulative retained and cumulative passing intersected. This point of intersection is referred to

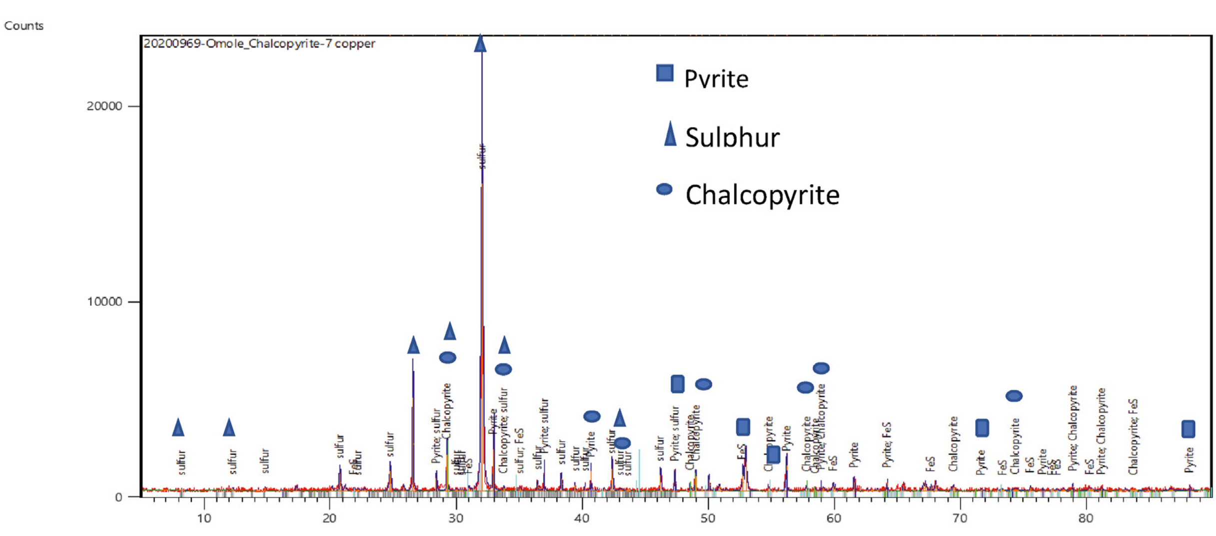


Fig. 4. X-ray diffraction pattern of the Nigerian chalcopyrite ore.

Table 2. Identified peak list of Nigerian chalcopyrite ore.

Compound name	Chemical name	Chemical formular	Percentage composition
Pyrite	Iron sulphide	FeS	49
Chalcopyrite	Copper iron sulphur	$CuFeS_2$	36
Sulphur	Elemental sulphur	S	13
FeS	Iron sulphide	FeS	1
Others	–	–	1
Total	–	–	100

as the economic liberation of the ore since the same set of sieves was used. At this point, valuable minerals had been unlocked to some extent from the gangue. Therefore, while concentrating the ore, to get a better yield, the sample must be pulverised to all passing 106 μm. Treating the ore mineral above this value may result in a waste of energy, time and resources because more valuable minerals may still be locked in larger sizes. Since froth flotation has been a reliable method for beneficiating chalcopyrite before extraction and purification, it is therefore appropriate to know the liberation size. Determining the liberation size with a guide to the sizes to be floated is very important because too fine particles will result in slime formation and reagent starvation, while coarse particles lead to poor liberation and flotation performance. This makes liberation studies very important in the concentration processes of ore.

3.1.1. Determination of Gaudin Schuhmann distribution

Gaudin Schuhmann distribution is a log–log plot of particle size analysis. It can be used to determine the 80% passing of the sieve products, especially in the study where non-uniform size distribution is involved. The determination of 80% passing is usually recommended widely in grindability studies and particle size distribution because after establishing the product size, this can be used to facilitate the routine control of the grinding circuit. Equation (1) below states the Gaudin Schuhmann distribution. Equation (1) below states the Gaudin Schuhmann distribution.

$$y = 100\left(\frac{x}{k}\right)^{a} \quad (1)$$

where y is cumulative % passing, x is screen size (particle size), k is mean particle size, and a is distribution modulus.

Taking the logarithm of each side of Equation (1) will result in Equation (2) below:

$$Log(y) = a.\log(x) + (2 - a.\log(k)) \quad (2)$$

A = a slope of the line

$(2 - a.\log(k)) = y$ intercept of the of the line

$$Slope = \frac{log\ 90 - \log 10}{\log 300 - \log 10}$$

$$= 0.67699$$

The size distribution of particles is expected to approximate a straight line (Fig. 3) if there is no problem in the crushing and grinding system.

3.1.2. Metallurgical balance for the Nigerian chalcopyrite ore

Table 1 shows the size distribution versus liberation and percentage distribution of the chalcopyrite ore. The assay values obtained from the results versus particles sizes are 11.17 in 300 μm, 11.53 in 212 μm, 11.83 in 150 μm, 11.91 in 106 μm, 12.16 in 75 μm and 12.82 in 63 μm. These results show that the copper content was distributed normally because the percentage of copper in the ore reduces with increase in particle size. It has also been reported that the highest metal content and percent distribution were recorded against particle size 63 μm, meaning that 63 μm is the actual liberation size of the copper ore [14].

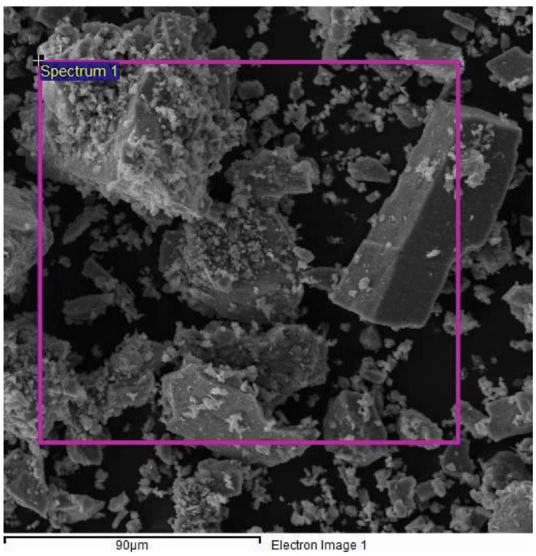
3.2. The X-ray diffraction pattern

The X-ray diffraction pattern shows that the ore contains chalcopyrite, pyrite and elemental sulphur

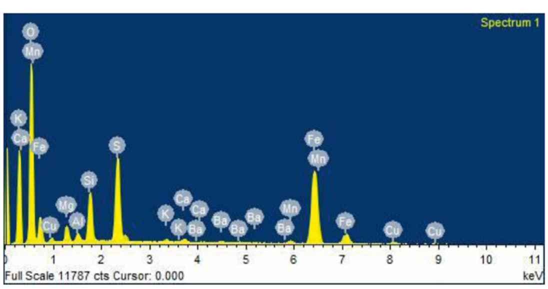
Table 3. Percentage content of compounds present in the Nigerian Chalcopyrite according XRF analysis.

Element	300 μm	212 μm	150 μm	106 μm	75 μm	63 μm
Na	0.01	0.05	0.04	0.05	0.06	0.06
Mg	1.79	1.53	1.54	1.60	1.75	1.80
Al	0.14	0.14	0.13	0.14	0.17	0.25
Si	0.50	0.45	0.41	0.43	0.48	0.63
P	0.01	0.01	0.01	0.01	0.01	0.01
S	2.58	2.51	2.61	2.67	2.87	2.99
Cl	0.02	0.07	0.07	0.08	0.08	0.09
K	0.01	0.02	0.02	0.02	0.02	0.03
Ca	1.22	0.62	0.61	0.65	0.61	0.61
Mn	1.38	1.41	1.41	1.41	1.35	1.33
Fe	51.85	52.56	52.28	51.93	51.23	50.10
Ni	0.25	0.29	0.27	0.27	0.26	0.01
Cu	8.92	9.21	9.45	9.52	9.72	10.24
Zn	0.03	0.03	0.04	0.03	0.01	0.09

(Fig. 4). The percentage composition of the identified pick list are 49% pyrite, 36% chalcopyrite, 13% iron sulphide as FeS and 1% elemental sulphur (Table 2). These results further confirm that the deposit is majorly dominated by pyrite and chalcopyrite. Nigerian chalcopyrite ore has been reported to contain pyrite as the major associated gangue [23,25]. It has been said that if the main copper mineral of a sulphide ore is chalcopyrite ($CuFeS_2$), then it can be easily processed than when it contains other minerals like chalcocite and covellite which makes it difficult to depress the pyrite inside.



Element	Weight %	Atomic %
O	43.43	67.23
Mg	2.43	2.47
Al	0.94	0.87
Si	5.60	4.93
S	10.62	8.20
K	0.35	0.22
Ca	0.48	0.30
Mn	0.96	0.43
Fe	32.78	14.54
Cu	1.76	0.69
Ba	0.64	0.12
Totals	100.00	



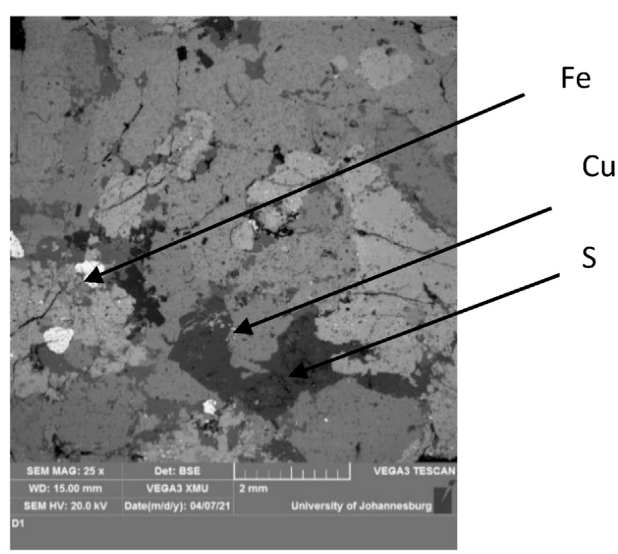


Fig. 5. SEM micrograph of the Nigerian chalcopyrite ore, including the spectrum, % composition and EDS image.

3.3. Percentage content of oxides present in the Nigerian chalcopyrite according to XRF analysis

Percentage composition by XRF shows that the major elements within the mineral vary with variation in the particle sizes (Table 3). The major compounds, according to XRF, are Cu and Fe. The presence of sulphur means that the deposit is a sulphide ore deposit of copper. The percentage composition of copper increases as the particle sizes reduces from 300 to 63 μm. The highest percentage of copper oxide is 10.24%, recorded against 63 μm. A high content of Fe in combination with S is confirms the presence of pyrite. Deposits of chalcopyrite are mostly found with pyrite as major associated gangue. There are other trace elements, which constitute impurities in the ore Mn, Si, Ca, Mg etc. XRF has been said to be a powerful analytical tool for the elecrochemical identification of nearly all the elements present in ores and minerals [21]. XRF has been reported to always detect major and minor components of ores and minerals, while XRD may only reveale dominant phases. The Nigerian copper ore has been reported to contain both chalcopyrite and pyrite while the content of pyrite is higher than that of chalcopyrite [23,25]. The implication of these is that the grade of the ore needs to be improved before extraction (see Table 4).

3.4. The micromorphology of the Nigerian copper ore

Fig. 5 shows the morphology of the Nigerian copper ore to contain large, medium, and small grains of mineral with varying irregular shapes. This is not unexpected for the sulphide ore [26–28]. The spectrum reveals the peaks, which include Cu, Fe, Mn, Al, Mg, Ca, Ba, K, Si, S, and O.The presence of Cu, Fe and S are indications that it is a sulphide ore of Fe and Cu. The impurities need to be removed before further extraction, therefore it can be concentrated by floth flotation before other smelting processes.

The EDS result of the SEM analysis of the head sample reveals that the ore contains mainly chalcopyrite, pyrite, and silica. Pyrite has been reported to be the major associated gang mineral of copper deposits, according to [26]. Larger copper deposits that contain up to 1% Cu are viable enough for Cu extraction. The minimum amount of metal in any deposit to make it an ore deposit varies from one metal to another. Ore from the non-ferrous metal deposit can contain as low as 1% metal. Copper ores may even contain lower than 1% [27]. According to [24] cut-off grade for copper with gold and silver has associated minerals can even be as low as 0.4% for open pit and 0.8% for underground mine. Therefore, the copper deposit can be viable since the weight % of Cu is up to 1.76%.

3.5. Chemical composition of Zamfara ore by atomic absorption photo spectrometry

AAS result test was performed with three trials, and the mean values were recorded to be 25.87% Cu, 32.05% Fe, 0.09% Mn, and 0.11% Pb. This means that copper and iron are major elements in the deposit, and it can be processed by flotation method to

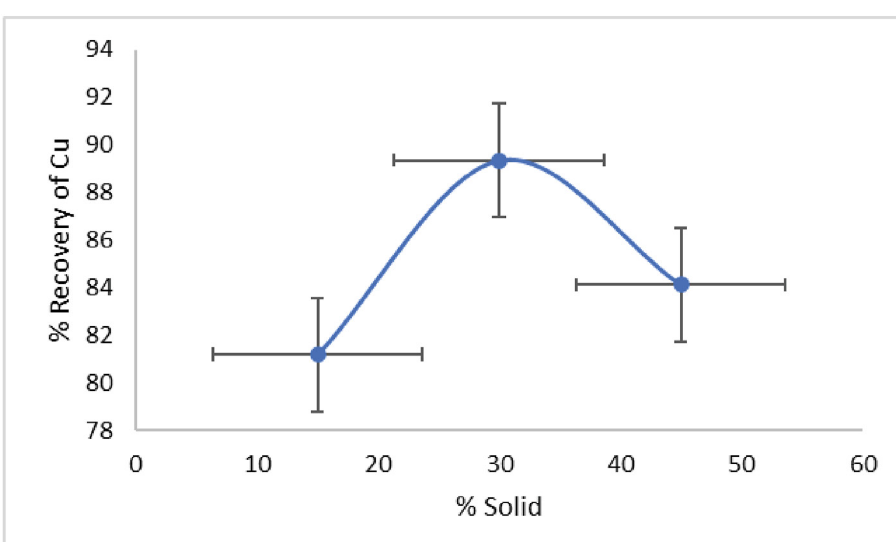


Fig. 6. Flotation response of the Nigerian chalcopyrite ore at varying % solids.

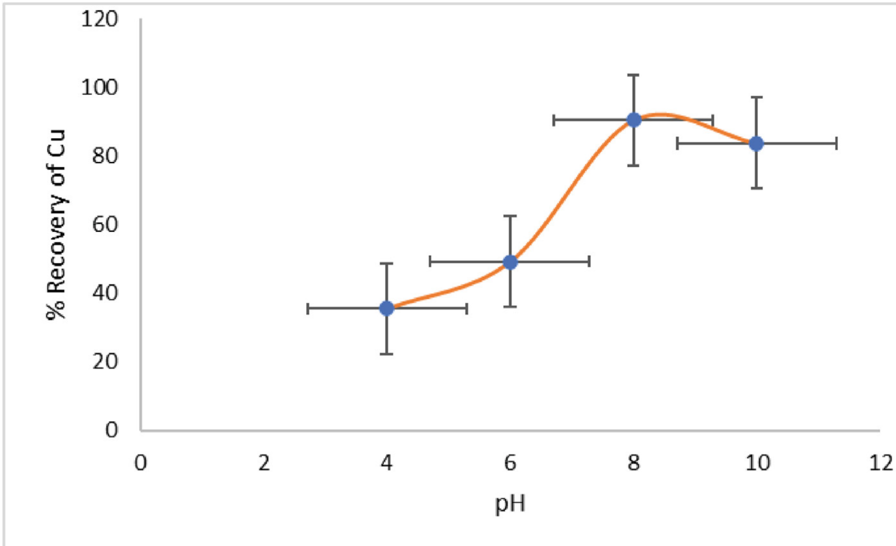


Fig. 7. Flotation response of the Nigerian chalcopyrite ore at varying pH.

reduce the bulk of iron, which will easily be depressed. Thereafter, the mineral can be transported for further extraction. Meanwhile, other elements are minor in the ore matrix. Mineralisation of deposits created by geochemical formation is said to have this nature [24,30].

3.6. Flotation response of the Nigerian chalcopyrite ore at varying retention time

Figs. 6–9 show the flotation response of the Nigerian chalcopyrite ore at varying % solids, pH, retention time and collector dosages. Fig. 6 shows the response of the Nigeria copper ore at varying % solids of 15, 30 and 45%. Recoveries at 15, 30 and 45% solids are 81.20, 89.37 and 84.14%, respectively, meaning that 30% solids gave the optimum recovery. Table 4 shows that the enrichment ratios and yields at 15% solid are 3.02 and 32.26% Cu, respectively. However, an increase to 30% solids increased the enrichment ratio and yield to 6.72 and 35.85% Cu while at 45%, there was a decrease in the yield (35.51) and increase in the enrichment ratio to 9.99. Therefore, maximum recovery and yield were recorded against 30% solid. There were not much difference between the recovery of valuables. However, since the highest recovery was recorded against 30% solid, it was therefore selected as the

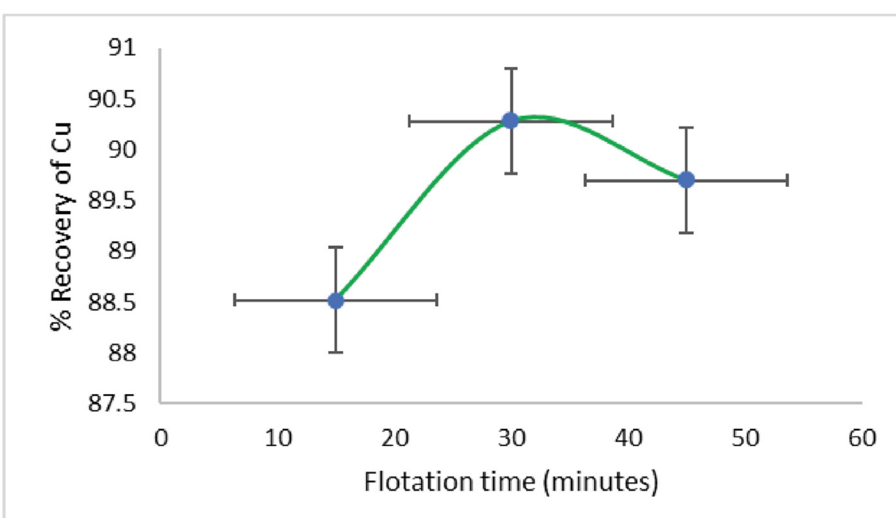


Fig. 8. Flotation response of the Nigerian chalcopyrite ore at varying retention time.

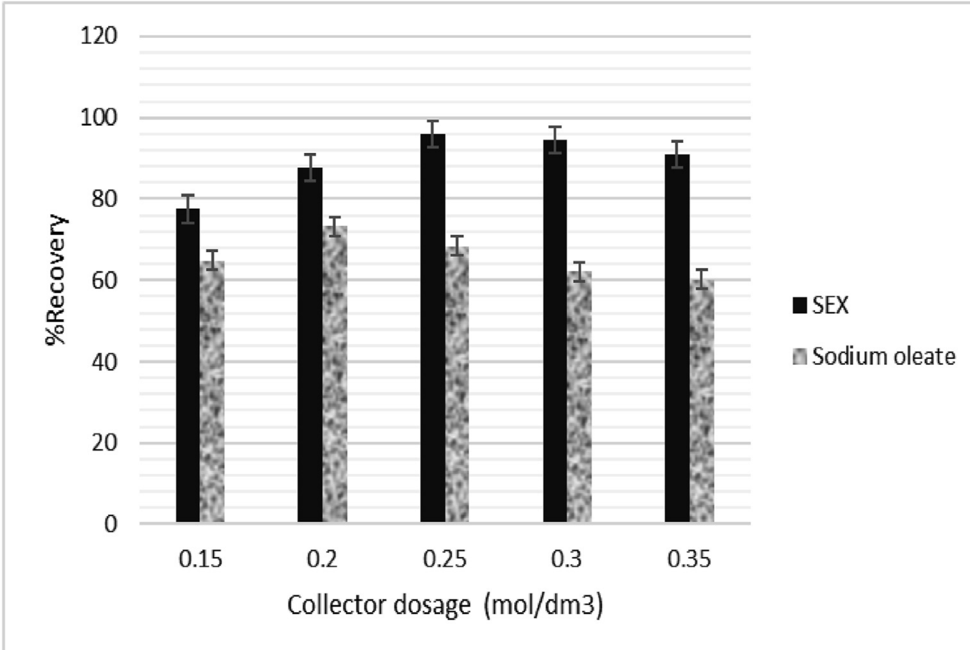


Fig. 9. Flotation response of the Nigerian chalcopyrite ore with sodium ethyl xanthate and sodium oleate at varying collector dosages.

optimum condition for the remaining flotation experiments.

Fig. 7 and Table 5 reveal the effects of varying pH on the flotation response of the Nigerian chalcopyrite ore. Recoveries at pH 4, 6, 8 and 10 are 35.50, 49.31, 90.46% and 83.74%, respectively, while the enrichment ratios are 4.53, 4.81, 6.66 and 6.52, and the yields are 24.18, 25.64, 25.51 and 34.75 respectively. This shows that the copper ore floats well in alkaline media. It has been reported that pyrites are depressed at high pH [29]. The Nigerian copper ore has pyrite as the major impurity. Therefore it is expected to record a high yield and enrichment ratio at high pH.

The effect of flotation (retention) time on the recovery of copper from the Nigerian low-grade copper was investigated at 15, 30 and 45 min, respectively. The pH and % solids were kept constant at 8 and 30%, respectively. Fig. 8 shows that recovery at 15 min was 83.74%, while at 30 and 45 min the recovery of 90.28 and 89.70% were recorded, respectively. The increase in enrichment ratio at 30 min retention time means more interaction between the reagents and the mineral, thereby making it cleaner. Whereas, by 45 min the time had become too long to give room for adverse reactions. Possibly, part of the depressed of the pulp were rendered hydrophobic (see Tables 6 and 7).

Table 4. Effect of % solids on the flotation response of the Nigerian chalcopyrite ore.

Variable		Feed weight	Feed assay	Conc weight	Conc assay	Recovery	Enrichment ratio	Yield (%)
% solid	15	120	12.8	38.71	32.22	81.20	3.02	32.26
–	30	240	12.8	86.05	31.90	89.37	6.72	35.85
–	45	360	12.8	127.84	30.33	84.14	9.99	35.51

Table 5. Effect of % pH on the flotation response of the Nigerian chalcopyrite ore.

Variable		Feed weight	Feed assay	Conc weight	Conc assay	Recovery	Enrichment ratio	Yield (%)
pH	4	240	12.8	58.04	18.79	35.50	4.53	24.18
–	6	240	12.8	61.53	24.62	49.31	4.80	25.6
–	8	240	12.8	85.22	32.61	90.46	6.65	35.50
–	10	240	12.8	83.41	30.84	83.74	6.51	34.75

Table 6. Effect of retention time on the flotation response of the Nigerian chalcopyrite ore.

Variable Retention time (min)	Feed weight (g)	Feed assay	Conc weight (g)	Conc assay	Recovery (%)	Enrichment ratio	Yield (%)
15.00	240.00	12.80	86.19	31.55	88.52	6.73	35.91
30.00	240.00	12.80	88.27	31.42	90.28	6.90	36.78
45.00	240.00	12.80	91.03	30.27	89.70	7.11	37.93

Table 7. Effect of sodium ethyl xanthate and sodium oleate at varying collector dosages on the yield and enrichment rato of the Nigerian chalcopyrite ore.

Collector dosage (mol/dm^3)	SEX		Sodium Oleate	
	Enrichment ratio	Yield	Enrichment ratio	Yield
0.15	2.33	33.20	1.87	34.59
0.20	2.36	37.15	2.12	34.56
0.25	2.38	40.38	1.95	35.12
0.30	2.37	39.93	1.69	36.82
0.35	2.34	38.86	1.66	36.33

After recording optimum parameters of 30% solids, pH of 8 and retention of 30 min, these were used to determine the efficacy of SEX and sodium oleate at varying collector dosages, and the results are shown in Fig. 9. SEX has been used by several authors to show good performance in the froth flotation of copper and many sulphide minerals. at 0.15, 0.2, 0.25, 0.3 and 0.35 mol/dm^3 using sodium ethyl xanthate, recoveries were 77.50, 87.72, 95.94, 94.49 and 90.90% respectively (Fig. 9). The enrichment ratios are 2.33, 2.36, 2.38, 2.37 and 2.34, respectively, and yields are 33.3, 37.15, 40.38, 39.92 and 38.86%, respectively. Using the same dosages of sodium oleate, recoveries were 64.75, 73.19, 68.46, 62.19 and 60.17%. Enrichment ratios were 1.87, 2.11. 1.95, 1.69 and 1.66, and yields of 34.59, 34.56, 35.12, 36.82 and 36.33, respectively. Summarily, sodium ethyl xanthate is more effective for the flotation of copper from the Nigerian copper ore, and is in agreement with [3].

After floating with 0.15 mol/dm^3 of SEX, the recovery increased to 87.71% from 77.50%, meaning the increase in dosage favoured hydrophobicity, making more valuable minerals to float because the grade also improved from 29.88 to 30.22. The grade and recovery were increased with further increase in collector dosage up to 0.25 mol/dm^3 (95.94%) but later decreased to 94.45 and 90.90% at 0.3 and 0.35 mol/dm^3. This means that hydrophobicity was no longer enhanced with the addition of an extra collector in the slurry [30].

4. Conclusion

The mineralogical, chemical and liberation characteristics as well as flotation response of low-grade copper ore (chalcopyrite) have been studied. Economic liberation was established to be $-150 + 106$ μm while 80% passing corresponds to 175.7 μm using the Gaudin Schuhmann equation. The particle size analysis shows that copper content was distributed evenly because percentages of copper in the crude reduces with an increase in particle size, and the highest % distribution was recorded against 63 μm. Major mineral phases in the ore are pyrite and chalcopyrite at 47 and 36%, respectively, while other minerals were present in traces. XRF results confirmed Fe and Cu as the major elements, while others are also in traces. SEM-EDS of the ore also revealed Cu as the major valuable mineral while Fe is the major impurity. The result of AAS shows an average of 25.87% Cu and 32% Fe in the ore, while Mn and Pb were present in traces. Optimum recoveries of copper were recorded at 30% solids, pH of 8, 30 min retention time and the highest recovery of 95.94% was recorded using SEX at 0.25 mol/dm^3. The flotation process has high potential in the concentration of low-grade sulphide copper ore from Zamfara state, Nigeria.

Ethical statement

The authors state that the research was conducted according to ethical standards.

Funding body

This research received no external funding.

Conflict of interest

The authors declare no conflict of interest.

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References

[1] Wirth H, Kulczycka J, Hausner J, Koński M. Corporate Social Responsibility: communication about social and environmental disclosure by large and small copper mining companies. Resour Pol 2016;49:53–60.
[2] Kalichini M, Corin KC, O'Connor CT, Simukanga S. The role of pulp potential and the sulphidization technique in the recovery of sulphide and oxide copper minerals from a complex ore. J. South. African Inst. Min. Metall. 2017;117(8): 803–10.
[3] Baba Alafara A, Ayinla Kuranga I, Adekola Folahan A, Ghosh Malay K, Ayanda Olushola S, Bale Rafiu B, et al. A review on novel techniques for chalcopyrite ore processing. Int J Min Eng Miner Process; 2012;1:1–16.
[4] Tanimoto AH, Durany XG, Villalba G, Pires AC. Material flow accounting of the copper cycle in Brazil. Resour Conserv Recycl 2010;55(1):20–8.
[5] Yan H, Yuan Q, Zhou L, Qiu T, Ai G. Flotation kinetics and thermodynamic behavior of chalcopyrite and pyrite in high alkaline systems. Physicochem. Probl. Miner. Process. 2018;54.
[6] Li S, Gu G, Qiu G, Chen Z. Flotation and electrochemical behaviors of chalcopyrite and pyrite in the presence of N-propyl-N′-ethoxycarbonyl thiourea. Trans Nonferrous Metals Soc China 2018;28(6):1241–7.
[7] Ziyan Wang, Jiwen Si, Zhenguo Song, Peng Zhang, Jian Wang, Yizhan Hao, et al. Precise and instrumental measurement of thermodynamics and kinetics of froth flotation by Langmuir-blodgett technique. Colloids Surfaces A Physicochem. Eng. Asp. 2020;605:125337.
[8] Huang X, Jia Y, Cao Z, Wang S, Ma X, Zhong H. Investigation of the interfacial adsorption mechanisms of 2-hydroxyethyl dibutyldithiocarbamate surfactant on galena and sphalerite. Colloids Surfaces A Physicochem. Eng. Asp. 2019;583:123908.
[9] Bonnet C, Seck G, Hache E, Simoen M, Carcanague S. Copper at the crossroads: assessing the interactions of the low carbon energy transition with a non-ferrous and structural metal. juillet: IFPEN/IRIS; 2019.
[10] Brest KK, Henock MM, Guellord N, Kimpiab M, Kapiamba KF. Statistical investigation of flotation parameters for copper recovery from sulfide flotation tailings. Results Eng 2021;9:100207.
[11] Cilek EC, Tuzci G. Flotation behavior of native gold and gold-bearing sulfide minerals in a polymetallic gold ore. Part Sci Technol 2021:1–9.
[12] Oyelola AO, Abdu DA, Victor AD, Igonwelundu MT, Bosan BM, Oyebode AB. Extraction of a low grade zinc ore using gravity and froth flotation methods. J Appl Sci Environ Manag 2016;20(4):903–8.
[13] Davenport WG. Copper production. Encycl. Mater. Sci. Technol. 2001:1671–80. https://doi.org/10.1016/b0-08-043152-6/00294-1.
[14] T IM, Bosan BM. Extraction of a low grade zinc ore using gravity and froth flotation methods * 1 ALABI OLADUNNI OYELOLA ; 2 DALHATU ABOKI ABDU, vol. 3. ABERE DARE; 2016.
[15] Taguta J. The thermochemical behaviour of thiol collectors and collector mixtures with sulphide minerals. University of Cape Town; 2015.
[16] O. O. Ola-omole and W. Nheta, "Comparative effects of mineralogical differences on the flotation behavior of complex sulphide ores".
[17] Bakalarz A. An analysis of copper concentrate from a kupferschiefer-type ore from legnica-glogow copper basin (SW Poland). Miner Process Extr Metall Rev 2021:1–13.
[18] Ajaka EO. Increasing economic EENEFITS from NIGERIAN minerals through accurate (compositional, analysis and processing. Int J Eng Sci 2010;2(1).
[19] Abdulfattah F, Rafukka IA, Manladan SM. Trends in characterization and beneficiation of non-ferrous metallic ores in Nigeria. In: Characterization of minerals, metals, and materials 2020. Springer; 2020. p. 47–55.
[20] Usaini MNS, Ali M, Usman HA. Determination of liberation size of Akiri copper ore, Nasarawa state. North-central Nigeria 2014;2(2):1444–52.
[21] Oyeladun OAW, Thomas DG, Yaro SA. Determination of the chemical composition and the work index of Rafin Gabas chalcopyrite ore. Niger. Min. J. 2012;10(1).
[22] Yerima ML, Abdulrahman AS. Physiochemical analysis of chanchaga ore, north Central Nigeria. J Appl Sci 2015;15(7): 1020.
[23] Hochella MF. Atomic structure, microtopography, composition, and reactivity of mineral surfaces. Miner. interface geochemistry 2018:87–132.
[24] Friedrich BM, Marques JC, Olivo GR, Frantz JC, Joy B, Queiroz WJA. Petrogenesis of the massive chromitite layer from the Jacurici Complex, Brazil: evidence from inclusions in chromite. Miner Deposita 2020;55(6):1105–26.
[25] Kinnaird JA, Bowden P, Ixer RA, Odling NWA. Mineralogy, geochemistry and mineralization of the Ririwai complex, northern Nigeria. J Afr Earth Sci 1985;3(1–2):185–222.
[26] Chimonyo W, Fletcher B, Peng Y. The effect of oxidized starches on chalcopyrite flotation. Miner Eng 2021;165: 106749.
[27] Wills BA, Finch J. Wills' mineral processing technology: an introduction to the practical aspects of ore treatment and mineral recovery. Butterworth-Heinemann; 2015.
[28] Olade MA. Mineral deposits and exploration potential of Nigeria. Prescott books; 2021.
[29] Bakalarz A. Chemical and mineral analysis of flotation tailings from stratiform copper ore from Lubin Concentrator Plant (SW Poland). Miner Process Extr Metall Rev 2019;40(6): 437–46.
[30] Asghari M, Nakhaei F, VandGhorbany O. Copper recovery improvement in an industrial flotation circuit: a case study of Sarcheshmeh copper mine. Energy Sources, Part A Recover Util Environ Eff 2019;41(6):761–78.