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Influence of mineralogy on biohydrometallurgical processing of complex sulphide ore

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Mineralogical characterization of Ishiagu (Nigeria) complex sulphide ore

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Abstract

A combination of SEM (Scanning Electron Microscopy) combined with Energy-Dispersive X-ray analysis (EDX), X-ray diffractometry (XRD), X-Ray Fluorescent (XRF) and Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used to characterize a bulk complex sulphide ore deposit in Ishiagu, in Ebonyin State, South Eastern part of Nigeria. A semi-geological study revealed characteristic hydrothermal vein deposits of the complex sulphide ore. Mineralogical analysis revealed the presence of siderite, sphalerite, galena, quartz, and traces of pyrite and copper bearing minerals. X-ray diffractometry showed that sphalerite mineral in the ore occurs as ferrous sphalerite with varied percentages of Zn and Fe within the various sizes. Scanning Electron Microscopy showed that the ore consist of fine to coarse grains, with less complex intergrowths of the constituent crystalline phases both at the interstitials and the boundaries with low interpenetrations.
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Keywords: Nigerian sulphide ore; Mineral morphology; Size and mineral distribution; Phase identification; Quantitative analysis

1. Introduction

The identification and characterization of minerals is of fundamental importance in the development and operation of mining and mineral processing systems (Hope et al., 2001), and it is very important in choosing a suitable flowsheet for recovering the constituent metals. It is also critical in optimizing actual plant for improving performance (Xiao and Laplante, 2004). According to Cook (2000), the growing need for detailed information about the mineralogical composition of a mineral deposit therefore determines that mineral characterization studies form an integral and often critical part of investigations of deposits. Knowledge of mineralogical/chemical composition, size, morphology and association with other minerals is therefore expected to provide insights and information on the characteristics, type, nature and amount of minerals and elements present within the ore at different locations that would permit an assessment and determination of the optimal processing route for its constituent minerals/metals. It has been developed to optimize the exploration of the mineral resource by providing a better knowledge of the ore characteristics and its behavior in the process (Sant'Agostino et al., 2001). Since different minerals from different locations within an ore deposit have different mineralogical compositions with different characteristics and complexities, their qualitative and quantitative distributions vary from location to location within an ore deposit, and from deposit to deposit, which could lead to variations in their recovery processes. Hence, complex sulphide ores have globally attracted the attention of researchers in different disciplines with totally different approaches and methods in characterizing complex sulphide ores (Eymery and Ylli, 2000; Kahn et al., 2001; Hope et al., 2001) for understanding the recovery processes of their constituent minerals and metals.

A large deposit of over 20 million tonnes of complex sulphide minerals (Table 1) is available in Nigeria, especially in Ishiagu (South Eastern part of Nigeria) and attempts have not

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Table 1
ICP-OES analysis (Wavelength emitted by each element)

Element	Zn	Fe	Pb	Cu	Si	S	Al	Cd	Co	Mg	Mn
Wavelength (nm)	202.5	259.9	220.3	224.7	212.4	180.73	396.1	226.5	237.8	280.2	257.6

been made to develop a suitable process for the optimal extraction of its constituent metals. The few research investigations on these ores which were centered on flotation studies (Onyemaobi, 1990) and on hydrometallurgy (Adebayo et al., 2003) did not take detailed applied mineralogical studies into consideration. Therefore, the underlying principles for understanding the recovery processes and interpreting the results obtained from their studies could not be fully understood. Several assumptions on the recoveries were made and reasons for poor recoveries could not be ascertained. Since detailed mineralogical studies would play an important role in overcoming wrong assumptions during process design and provide a sound background in understanding the behavior of the minerals during beneficiation and recovery processes, it is therefore of paramount importance that a detailed mineralogical study of these ores be carried out. Moreover, since the goal of every mineral processing operation is to effectively separate the valuable material from the gangue with minimum metal loss in tailings, the need to have a full understanding of mineralogical knowledge of the ore deposit is imperative to develop and employ a sustainable, effective and relatively economical recovering route. This study is therefore aimed at characterizing a complex sulphide ore deposit located at Ishiagu South Eastern part of Nigeria with a view to provide mineralogical background that could aid the understanding of the recovery processes of its constituent metals.

2. Geology of Nigerian sulphide ores

2.1. Regional geology

The Benue trough of Nigeria (Fig. 1) is a continental-scale intraplate tectonic megastructure which is part of Mid-African Rift System and its genesis is connected to the opening of the Equatorial Domain of the South Atlantic, which was initiated in the latest Jurassic–Early Cretaceous (Maluski et al., 1995). According to Akande et al. (1989), the veins in the lower Benue trough consist of complex sulphide and associated minerals hosted by carbonaceous shales, while those in the upper trough are hosted by limestone and sandstone. These complex sulphide ore deposits are mostly found in cretaceous sedimentary rocks within the lower and upper Benue trough and extend over 600 km stretching from Ishiagu in the South-East to Gombe State, North East of Nigeria (Onyemaobi, 1990).

Despite the fact that there is an abundance of these mineral deposits within the trough, and their existence has been known for a long time (Akande et al., 1989; Maluski et al., 1995), only a few are presently being exploited at different low levels by ineffective small scale private entrepreneurs. Moreover, no attention has been paid by the small scale exploiting entrepreneurs to the study, determination and evaluation of the mineralization of these ores at various locations. This non-effective exploitation and processing technologies of these minerals has made them a burden and therefore requires that a detailed study of their mineralogical compositions and characteristics be known to enhance sustainable development.

2.2. Description of the Ishiagu complex sulphide ore deposits

Ishiagu is located at Latitude 6°05′34″–6°09′28″N and Longitude 6°30′46″–6°51′28″E, about 20 km South-East of Enugu and 10 km South-West of Afikpo, in the South Eastern part of Nigeria. About 4 km to the South-East of Ishiagu are several ridges of deposits of complex sulphide ores which extends all through the lower Benue trough. The ores are mostly found along fault/fractures and fissure openings within the sedimentary rocks which occurred in the form of veins and veinlets which are several centimeters to a few meters thick, and are several hundreds of meters long and extend very deep. They have strike lengths of kilometers and up to tens of meters wide, and vary from trace lengths of meters to hundreds of meters and widths of centimeters to a few meters. Physical examination of the ore deposits at different locations and different points within the mine sites also shows variations in the compositions of the bulk ore with varying degrees of richness in galena, sphalerite and siderite.

For this study, representative samples of the bulk complex sulphide ore deposit were collected from two small scale mining companies at three different locations. Mineralogical characteristics of these samples were investigated with reference to the mineral phases identification, mineralogical composition and elemental composition using Scanning Electron Microscopy combined with Energy-Dispersive X-ray analysis, X-ray

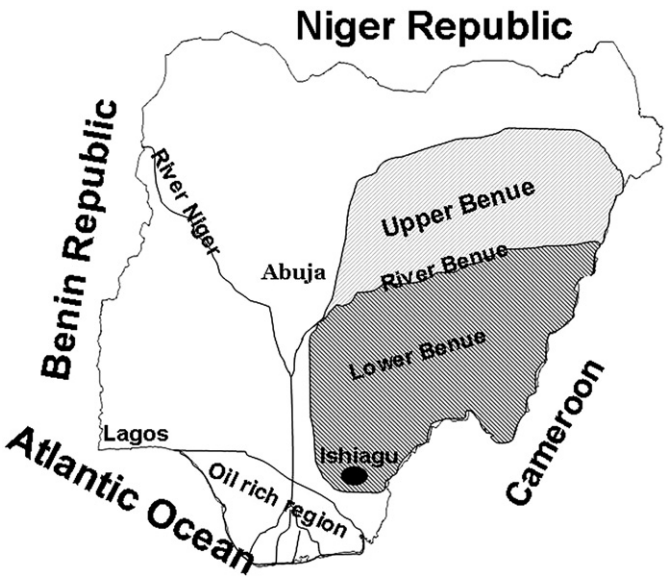


Fig. 1. Map of Nigeria showing areas of complex sulphide ore deposits.

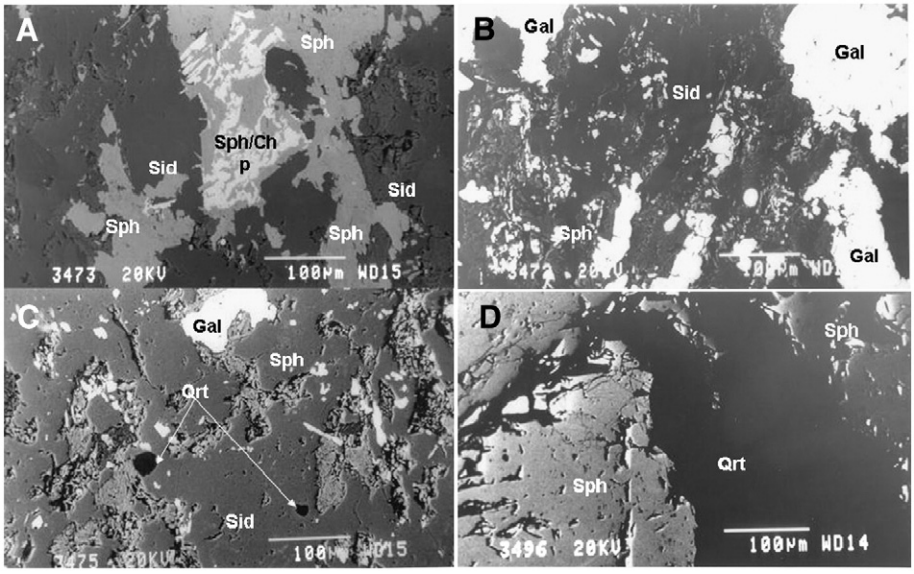


Fig. 2. SEM/BSI micrographs of the bulk ore showing morphologies and intergrowths of sphalerite (sph), chalcopyrite (chp), siderite (sid), galena (gal), and quartz (qrt).

diffractometry, X-Ray Fluorescent, and Inductively Coupled Plasma-Optical Emission Spectrometer.

3. Characterization methods

3.1. Scanning Electron Microscopy (SEM) analysis

Morphological and qualitative analyses of the bulk ore were performed using SEM-EDX. The SEM provided information on the physical properties of minerals, while EDX provided information on their chemistry. Scanning Electron Microscopy studies for mineral analysis of representative samples were conducted in two stages using SEM model JEOL 840. All the samples were carbon coated in order to make the minerals surface conductive. Samples for analysis were cut, polished, mounts in embedded epoxy resin, and finally polished to obtain a mirror-like surface. The polished surfaces were finally carbon coated before analysis. Qualitative chemical analyses of minerals were carried out on some mounts of the ore using (SEM/EDX) to produce Backscattered Images (BSI).

3.2. Size and minerals distribution and liberation

The ore was staged crushed in a cone crusher and 0.5 kg of the crushed ore was ground for 15 min in a rod mill consisting of 10 rods of 460 g each. Size analysis of the ground products was carried out to determine the quality of each grinding using the sieve analysis method in a laboratory test sieving. The distribution of elements within the size ranges was analyzed using XRF and ICP-OES, while mineral phases were identified with XRD. Mineral liberation was assessed using SEM/EDX analysis on the particles in the size fractions. A total of 5 micrographs from each of the size fraction were observed. The degree of the liberation of the mineral phases was estimated using the following equation:

$$\%\text{Mineral liberation} = \frac{\text{FM}}{\text{FM} + \text{LM}} \times 100 \quad (1)$$

FM Total area of mineral particles occurring free

LM Total area of mineral particle in locked form.

3.3. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) analyses were conducted for the qualitative and quantitative analyses (phase identification) of the minerals within the ore, using the powder method. Phase identification of the mineral constituent of sizes −53, 53, 75, and 106 μm, was determined by X-ray diffractometry using Philips PW 1830 X-ray diffractometer with a Cu-anode. The X-ray diffractometer was operated at a generator voltage of 40 kV and a current of 20 mA with the goniometer 2θ values varying from 0° to 80° at a scan rate of 1.0 s/step. For quantitative analysis of the bulk ore, 2 g each of the particle sizes of sizes −38, 38, 53, 75, and 106 μm was mixed together and further grounded to fine powder. The quantitative analyses of the ore were carried out using X $^{//}$Pert PRO Diffractometer by PANanalytical, operated at 40 kV and 40 mA for 30 s. High Score Plus software was used for quantification of the constituent minerals.

3.4. X-ray Fluorescence Spectroscopy analysis

Quantitative analysis of the major elemental within the ore was determined by X-ray Fluorescence Spectroscopy using Magi $^{//}$X Pro XRF spectrometer by PANanalytical. A mass of 10 g each of the particles of sizes of −38, 38, 53, 75, and 106 μm, was mixed together and further ground to powder. 8 g of the mixed powdered ore sample was mixed with 2 g of Herzog organic binder. The organic binder contains 90% cellulose and 10% wax. The mix was further ground and homogenized using a mill. The homogenized samples were placed in an aluminum cup and hydraulically pressed into pellets under a very high pressure of 20 tonnes for 60 s. This was done to ensure sample integrity under the vacuum and a consistent surface to receive the X-rays. Quantitative analysis was carried out with the Magi $^{//}$X Pro XRF spectrometer at 4 kV, using IQ^{+} "Standardless" analysis.

3.5. Optical Emission Spectroscopy analysis

Quantitative analysis of the minor elements within the ore was performed by Optical Emission Spectroscopy method using ICP-OES model SPECTRO CIRO. 10 g each of the particles of sizes of −38, 38, 53, 75, and 106 μm, was mixed together and further ground to powder. 2 g of the homogenized sample was digested in nitric acid and hydrofluoric acid in a microwave, followed by dilution and analysis. Sets of calibration standards were prepared and the calibrating solutions were sprayed into the plasma. Suitable lines from the specific wavelength emitted by each element (Table 1) were measured by means of a charged couple device, and each metal was quantified from a standard curve.

4. Results and discussions

4.1. Mineral phases, morphologies, and liberation

The mineral phases identified by SEM/EDX analysis through Backscattered Images (BSI) are shown in Fig. 2. The major mineral phases constituted essentially siderite, sphalerite, galena, quartz and chalcopyrite minerals. Other

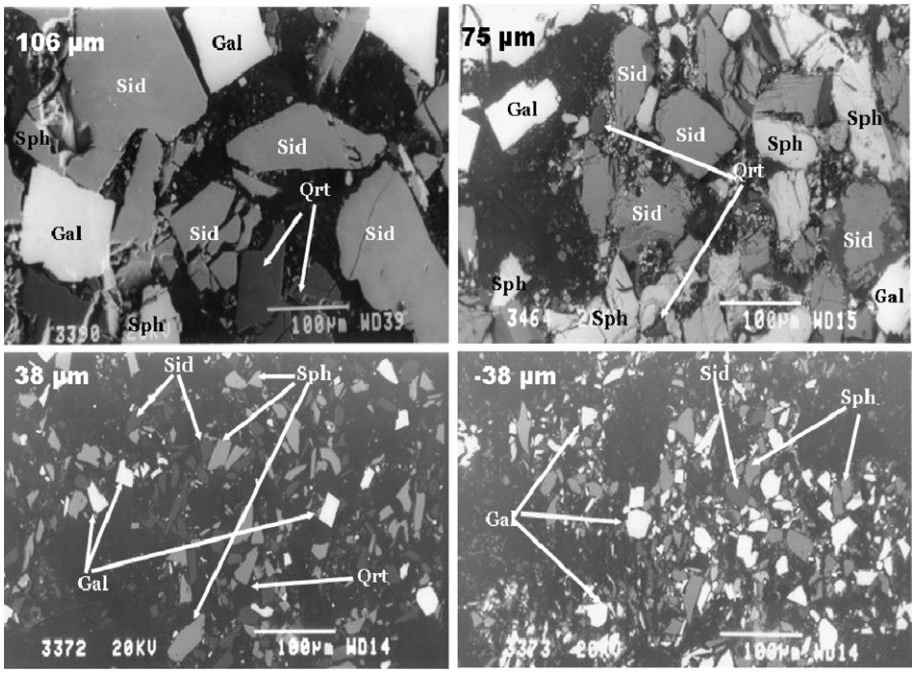


Fig. 3. SEM micrographs of particle sizes 106, 75, 38 and −38 µm showing mineral liberations.

minerals occurred as trace minerals and were not recognized by image analysis, similar to the analysis by Kahn et al. (2002). The ore shows a characteristic hydrothermal complex sulphide deposit nature of fine to coarse grains intergrowths of the constituent crystalline phases (Vujanovic, 1974). The sphalerite occurs as crystalline masses and is characterized by light grey colour, while galena occurs as medium to coarse crystalline masses similar to the Dereiçi, Turkish copper–lead–zinc deposits studied by Soylu and Erler (1999).

Fig. 2A shows the intergrowths of chalcopyrite mineral (lighter grey) with sphalerite (light grey), and the intergrown of quartz (black) with siderite (dark grey). Fig. 2C shows the complex intergrowth nature of the ore with grain boundaries of sphalerite, galena (white) and quartz intergrown together with siderite. Fine-grained and complex intergrowths occur between siderite, sphalerite and galena (Fig. 2B), while fine intergrowths occur at the interstitials and boundaries of sphalerite and quartz (Fig. 2D). The intergrowth nature of the constituent minerals would have resulted from the precipitation, crystallization and growth of the minerals caused by fluid flow pattern and diffusional transportation of vein forming minerals. It would have also resulted from the alteration assemblage that probably formed during precipitation within the fractures that provided channelways for hydrothermal fluids. Although there are several intergrowths among the mineral phases, the fine to coarse structure of the phases will aid easy liberation of the constituent mineral phases. This ease may be promoted by the differences and combination of both transgranular and intergranular fracturing liberation, which might cause grains to be released perfectly. Moreover, the intergrowths are less complex and the grain boundaries have little interpenetrations.

The SEM/EDX micrographs of some of the size fractions shown in Fig. 3 revealed the mineral liberation characteristics of the ore. It is clearly shown that the ore exhibits a high degree of mineral liberation (Fig. 4). Very good mineral liberation was attained at 75 µm, as individual component minerals were distinctly separated. This revealed that, grinding the ore finer than 75 µm may not necessarily lead to higher recovery, but will lead to a mere over grinding. This would also result in increased production costs that will be incurred from over milling. Since the behavior of particles in separation processes is a function of different properties of the particles, it is expected that grinding the ore to 75 µm, will assure the required concentrate grades with reasonable mineral recoveries. The ease of the liberation of the constituent mineral could be attributed to the fine to coarse structure of the mineral phases. This ease may be promoted by the differences and combination of both transgranular and intergranular fracturing liberation, which might cause grains to be released perfectly. Moreover, the intergrowths are less complex and the grain boundaries have little interpenetrations, which promoted the release of minerals.

4.2. Qualitative and quantitative analyses studies

The diffractogram (Fig. 5) shows a typical X-ray diffraction pattern of the ore. First, the background and peak positions were identified and based on the peak positions and intensities a search-match routine was preformed. Generally, there are matches of line of mineral phases. The matching of lines of mineral phases could be that some of the minerals must have precipitated from the same fluid. This in conjunction with phase disorientation could result in overlapping effects of the minor minerals with those of the major minerals. The peaks of the minor mineral phases might occur at the same or in the neighborhood of locations as the peaks of the major phases, thereby leading to inaccuracy in resolving the peaks.

Careful XRD investigation revealed that the sample is composed of siderite, sphalerite, galena, quartz, and traces of copper occurring as stannite at smaller particle size fractions. At higher particle sizes fractions of 75 and 106 µm, copper occurred as defect chalcopyrite group mineral with chemical formula

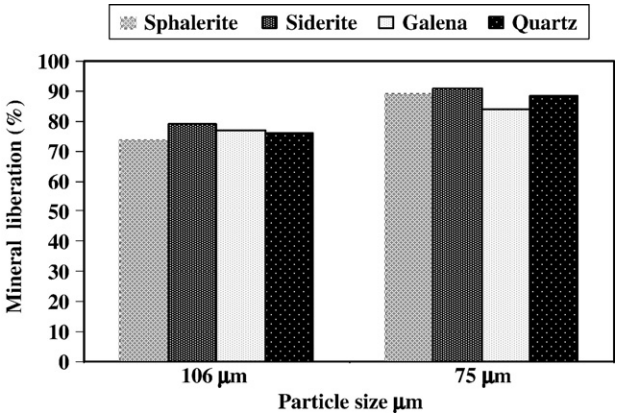


Fig. 4. Relative mineral liberation at particle size fractions of 106 and 75 µm.

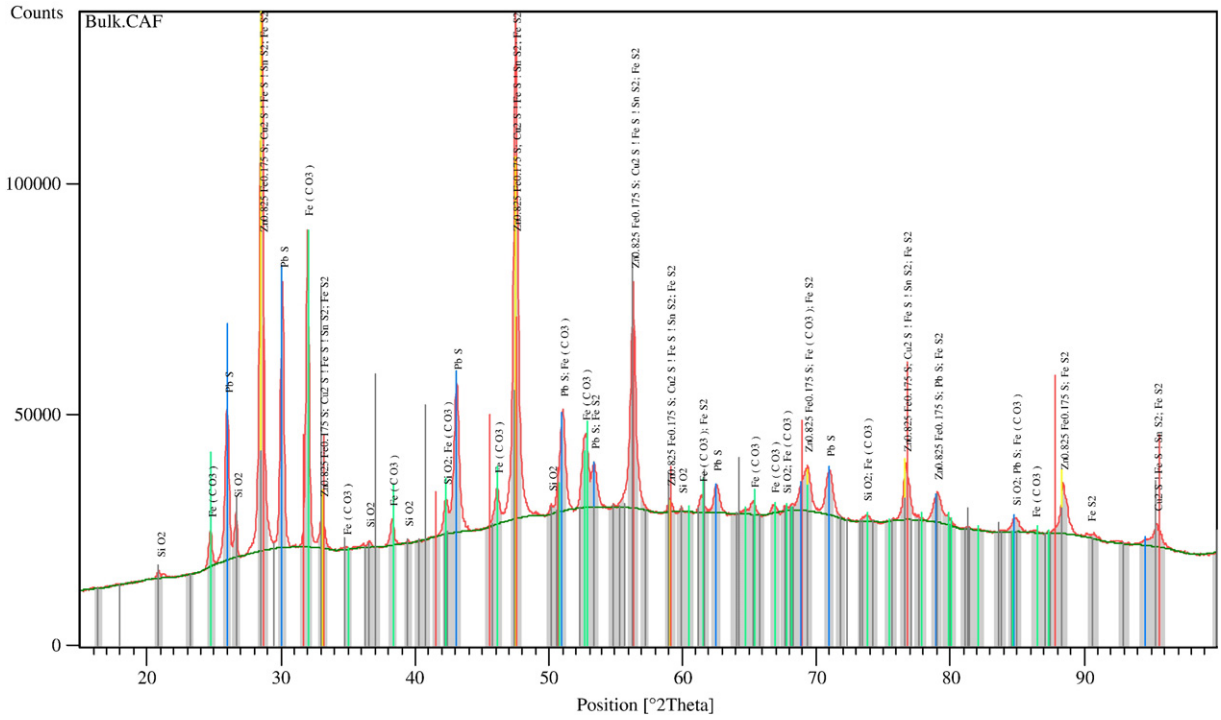


Fig. 5. Typical diffraction pattern of the ore showing the minerals identified.

Cu_2MnSnS_4. SEM/EDX analysis of the polished surface of the bulk ore before grinding shown in Fig. 2 revealed that copper was found as chalcopyrite, which was similar to the chalcopyrite group mineral defect chalcopyrite group mineral identified at particle sizes of 75 and 106 μm. The occurrence of chalcopyrite at higher particle size fractions and stannite at lower particle size fractions might result from the similarity in the crystal structure of defect chalcopyrite and stannite. According to Lowe-Ma and Vanderah (1991), both chalcopyrite and stannite structures are ordered (tetragonal) versions of sphalerite having no vacancies, so their defect forms result in a similar structure. McDonald (1967) noted that an alteration on the assemblage of sulphide ore occurring during metamorphism could lead to textural and mineralogical changes, generation of new or additional phases, and the redistribution of major and minor components. Therefore, the thermodynamic instability in mineral phases caused during hydrothermal formation, precipitation and possibly through metamorphism might also cause some phase change that could probably occur during processing. The similarity in their crystal structure and the probable phase change together with their trace amounts in the ore might lead to the inconsistency in the identifications by XRD.

The sphalerite in the ore occurs as ferrous sphalerite. The presence of iron in the sphalerite might be probably due to availability of iron in the hydrothermal fluid as the sphalerite crystal growths. This process occurs by a reaction of the diffusing zinc ions transported in hydrothermal solutions with iron, where the oxidation of Fe^{2+} to Fe^{3+} accelerates the reaction of diffusing zinc with Fe^{3+}. The amounts of iron are dependent on the temperature and chemistry of the environment (Lusk et al., 1993). It was observed that there were variations in the chemical composition of ferrous sphalerite through variation in the ratios of zinc to iron at different particle sizes (Table 2), with finer particles having lower percentages of iron. A similar situation was observed by Zielinski et al. (2000), where coarser sphalerite grains containing more solid solution iron was attributed to presence of different generations of sphalerite in the deposit that caused variations in sphalerite composition in the ore body. It is therefore believed that the hydrothermal melt forming the ferrous sphalerite in the ore deposit in this study might have crystallized over a range of temperatures and pressures, thereby forming an overlap of sphalerite phases with variations in their iron content. The difference in the solid solution iron at different size fractions might also be as a result of structural imperfections (Langfordy and Louerz, 1996) resulting from differences in fineness to coarseness of the particle having uneven smooth plane surfaces, leading to peak intensity errors (Connolly, 2003).

Rietveld analysis indicates that the ore contains 42% siderite, 35% sphalerite, 11% galena and 8% quartz. The percentage composition pyrite and copper bearing mineral could not be accurately determined by Rietveld analysis. This might be due to the fact that the relative amount is less than 2%. According to Kile and Eberl (2000), while X-ray diffraction can be very accurate in quantifying major components within a mixture, it is not very good at detecting

Table 2
Variations in Zn and Fe in sphalerite within particle sizes

Particle size	Chemical composition of sphalerite
106 μm	$Zn_{0.721}Fe_{0.279}S$
75 μm	$Zn_{0.776}Fe_{0.224}S$
53 μm	$Zn_{0.785}Fe_{0.215}S$
38 μm	$Zn_{0.825}Fe_{0.175}S$
−38 μm	$Zn_{0.825}Fe_{0.175}S$

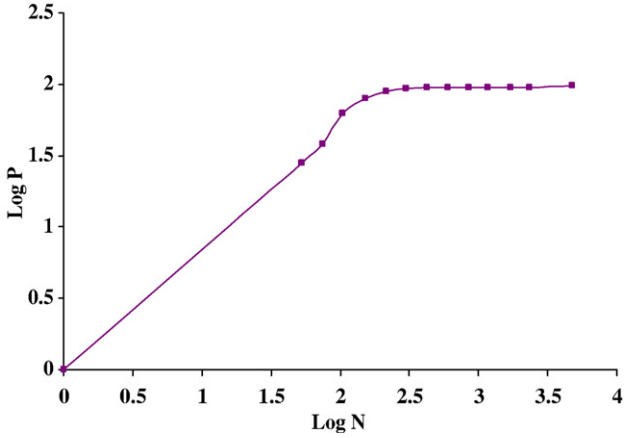


Fig. 6. Gate Gaudin–Schuhmann size distribution of the grinding routes.

Table 3
% composition and distribution of the elements

Sample	XRF						ICP-OES					
	O	Zn	Fe	S	Pb	Si	Mn	Cu	Mg	Ca	Al	Cd
Bulk ore	31.33	25.53	12.59	13.82	9.78	4.79	0.94	0.45	0.48	0.37	0.27	0.091
106 μm	33.33	26.63	11.98	13.55	9.02	3.02	0.89	0.52	0.44	0.34	0.15	0.099
75 μm	32.71	25.81	12.23	13.67	9.45	3.10	0.90	0.47	0.45	0.35	0.22	0.091
53 μm	32.61	25.05	12.96	13.91	10.15	4.23	0.91	0.42	0.52	0.37	0.28	0.088
53 μm	33.01	24.51	13.11	14.03	10.41	5.51	0.97	0.39	0.53	0.38	0.39	0.088

constituents that are present in minor amounts (less than about 2%). Hence, determination of relative amount of the constituent element of the trace minerals was done by XRF and ICP-OES.

4.3. Size and minerals distribution characteristics

The effectiveness of practically all mineral processing and extraction processes is a function of the size of the particle treated. Because of the comparatively high cost of size reduction (Benzer, 2005), and the difficulties associated with separating minerals when over or under liberation occurs, it is essential that the correct amount of size reduction be achieved. The results of the size analysis presented in Fig. 6 show that the particles are evenly distributed among the size ranges. The particles were mostly distributed in the size range of +75 −38 μm. 31.01% of the total mass of the ore are retained at the particle sizes between 106 and 300 μm, 54.14 are retained at less than 75 μm, while 14.85% are retained at above 300 μm.

Particle size analysis is of great importance in the design of an optimal process for mineral processing and extraction, and several studies have been carried out to determine its effects on mineral recovery (Ozcan et al., 2000; Hossain et al., 2004; Deveci et al., 2004). It is observed, however, that particle size alone may not reveal enough information about a process to allow process optimization (Barrett, 2003). Although particle size analysis provides information on measuring the extent of the liberation of the value minerals from the gangue at various particle sizes and determines the optimum size of feed to the process for maximum efficiency as well as the size range at which any losses are occurring in the plant so that they may be reduced, it does not provide detailed information on the distribution of the constituent minerals and elements within the various size ranges to ascertain the degree of the reduction of specified minerals (Olubambi et al., 2006). While they are useful for characterizing and determining efficiency, they offer little information about the breakage characteristics of the material within the comminution system (Fuerstenau et al., 1999). Therefore, to provide information for understanding ore breakage from a mineralogical view point and provide additional information for which a mineral recovery could be understood, elemental analyses of the bulk ore and within the various size ranges were analyzed.

The results of the XRF and ICP-OES quantitative analysis of the elements in the bulk ore and within the sizes are shown in Table 3. There was inaccuracy in the quantification of the minor elements in the ore by XRF as the quantification results obtained were inaccurate and too low for the minor elements, and could not be used to ascertain their actual composition. Since the quantification results for the minor elements obtained from XRF analysis were inaccurate, the minor elements were determined using ICP-OES. Zinc, the major metal present in the ore representing 25.5% of the bulk ore, reduces in amount as the particle size reduces while lead representing 9.78 is observed to occur in higher amounts in larger particle sizes. The amounts of iron and quartz reduce as particle size reduces, while copper increases. The observed elemental distribution pattern is presumed to be a very essential data in mineral and metal recovery process. According to Kahn et al. (2002), it is helpful in showing the relative amount of individualized grains that derives from the valuable mineral phase available for processing.

The variation in the distribution of elemental composition within the different particle sizes could be attributed to ore mineralogy as minerals' response to breaking is largely determined by their mineralogical properties. Sphalerite has a dodecahedral cleavage but fractures on uneven–flat surfaces, hence, during grinding, sphalerite fractures only along the flat surface, resulting in flat particles which pose difficulties in reduction even at higher grinding. Galena has a good cleavage and fracture, and therefore easily breaks along its cleavages into cubes. This ability to break along its cleavages with its softness and brittleness properties makes its size reduction easy. The increase in silicon content at particles of lower sizes could be traced to the mineralogical properties of quartz. Quartz is hard and very brittle, and therefore breaks easily into fine particles, due to its good fracture, even though it has no cleavage. An increase in the amount of sulphur at lower particle sizes could be attributed to the increase in the degree of deformation, which caused some structural changes and transformations. This was also observed by Hu et al. (2004), where a greater amount of new lattice defects were produced on the surface of mechanically activated pyrite because of the formation of elemental sulphur during mechanical activation and the extremely incomplete cleavages.

5. Concluding statements

The mineralogical studies of Ishiagu (Nigerian) bulk complex sulphide ore have shown that the complex ore is made up of sulphide, carbonate and oxide typically consisting of sphalerite, galena, siderite, and quartz. Sphalerite occurred as ferrous sphalerite with crystalline masses and is characterized by dark grey colour, while galena occurred as medium to coarse crystalline masses.

The ore showed fine to coarse grain intergrowths of the constituent crystalline phases both at the interstitials and the boundaries. The fine to coarse structure of the mineral phases combined with their transgranular and intergranular nature promoted the ease of the liberation of the constituent's mineral phases at particle size fraction of 75 μm.

The results of this characterization study have provided relevant mineralogical information on which the processing of the ore could be easily achieved. However, since ore deposits are heterogeneous in nature, it is recommended that further characterization studies on this ore deposit be done and constantly repeated, in order to ascertain its constituent and the changes in its mineralogy at other location and as it undergo successive exploitation.

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