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Processing and characterization of chalcopyrite (CuFeS_2) sample from Botswana

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Abstract

Beneficiation of chalcopyrite and most minerals in general requires specific conditions and raw materials based on characteristics of the mineral to optimize processing hence income. Therefore characterization of minerals is an important aspect in mineral processing. In this investigation X-ray diffraction (XRD) and Scanning Electronic Microscope (SEM) techniques were applied on a sample of chalcopyrite. XRD was mainly applied to obtain phase compositions, lattice parameters hence the crystal structure and its amorphous nature. The XRD intensity peaks obtained were analyzed using Match3 software which showed the sample to contain phases of CuFeS_2 as a dominant compound, also phases of clinocllore which is Fe-rich (in the form of Fe and FeO) where observed. The mineralogical analysis showed other relatively small peaks which reflect less dominant compounds such as calcite, TiC , Yoshiokaite etc. From this CuFeS_2 data, the lattice parameters obtained where $a = 5.229 \text{ \AA}$ and $c = 10.422$ (Tetragonal lattice). These represent the compound in its natural state. Chemical analysis determined by Energy dispersive XRD analysis (SEM) revealed elemental compositions of Cu, Fe and S as 31.02, 33.07 and 34.08 wt.% respectively while majority other occurring elements averaged at <0.2 wt%. XRD information is valuable in mineral processing or extraction of concentrations. Gangue materials affect the recovery/beneficiation of chalcopyrite during hydrometallurgical or pyrometallurgical processes. In SEM analysis the surface properties such as presence of surface films are closely linked to stability of a material during hydrometallurgical processing hence determination of leaching agents is dictated by such information. Based on XRD and SEM analysis on characteristics of chalcopyrite a possible processes route can thus be identified mainly to recover iron that can be used as an alternative feed material for steelmaking plants particularly to replace scrap steel.

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1. Introduction

Chalcopyrite is the name given to the copper iron sulphide mineral. Chalcopyrite is derived from the 2 Greek words “chalkos” and “pyrites” meaning copper and strike fire respectively [1]. Chalcopyrite minerals are considered to be

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one of the most diverse and important minerals with great chemical, physical and structural properties. Chalcopyrite appears in nature as a primary mineral in massive displacements, hydrothermal veins and as an ex-solution product in igneous rocks such as the mafic etc. Reactions of sedimentary rocks subjected under redox reactions can also result in formation of chalcopyrite [2]. The main constituents are Copper (Cu), Iron (Fe) and the sulfide (S_2). Analytical studies have also shown existence of relative small quantities of elements such as zinc, lead, nickel etc. It is the most stable metal sulfide existing to have a face-centered tetragonal system therefore separation of the element sulfur from the mineral requires careful control and adjustment of leaching conditions [3].

Beneficiation is the current practice applied in chalcopyrite ore processing and most ores. Beneficiation also termed ore dressing is the first step in mineral processing after the mineral in question has been recovered from the ground. In this process the ore is prepared and liberated, grains of the ore are mechanically separated from gangue minerals such that a concentrate containing most of the mineral is produced together with tailings or discard containing a series of gangue material [4,5]. Processes that can be used in beneficiation of chalcopyrite are pyrometallurgy and hydrometallurgy. Hydrometallurgy is also widely known as the leaching process where chloride leaching is incorporated to the mineral cake and metal are extracted from leach solutions. In pyrometallurgical processes chalcopyrite is heated to high temperatures in the presence of oxygen.

Planning, Optimization, and monitoring of mineral chalcopyrite is one of the important aspects in mineral beneficiation hence the need for characterization is fundamental in mineral processing. A proper mineralogical analysis does not only entail elements of economic value but also those that are detrimental and their occurrence can affect beneficiation and final products. The choice of a process route and raw materials to use is also dependent on other elements that core-exist with the compounds or elements of interest determined through chemical analysis hence characterization in general can add value in mineral optimization hence income [6]. In addition selection of correct raw materials during extraction can help solve or rectify environmental problems at an early stage. Chalcopyrite is really a fascinating mineral and like most minerals its constituents, phase distributions, morphology etc. can vary depending on geological location. Understanding chalcopyrite through characterization especially elemental composition is key in knowing dissolution kinetics and passivation mechanisms during ore processing because respective ions of constituents are involved in reactions during leaching [7,8]. Researchers have used different analytical techniques such as scanning electron microscopy and X-ray diffractometers to characterize chalcopyrite mineral with fine particles size, low crystallinity with a small portion of the mineral phase. E.R. Mejia et al conducted the chemical analysis on mineral chalcopyrite using a UV-visible GENESYS™ 10 spectrophotometer hence the determining the weight percentage (wt. %) of copper, Iron, Sulphur and other elements [9]. Mejia's study also includes the measurements of pH and redox potential of chalcopyrite. This knowledge is critical in developing an understanding of chalcopyrite dissolution kinetics during leaching as a step in hydrometallurgical processing. Other studies on characterization of chalcopyrite includes the work of Yund et al, (1996) who studied chalcopyrite phases of Cu-Fe-S system hence deterring its stability. The study of Cu-Fe-S phase systems goes as far as 1917 by Burdick and Ellis who came up with the 1st two model structures of chalcopyrite using X-rays [10].

In this work a crystal of chalcopyrite is prepared into powder through crushing and pulverization and characterized. The fundamental aim of this investigation is to obtain elemental compositions and phase analysis of chalcopyrite from Botswana by using XRD and SEM. Furthermore to obtain information about morphology, structure, composition and phase and/ elemental distribution EDX of SEM, match3 and debugging software's of XRD are used. Knowing such information through these analyses can help maximize processing especially in the recovery of iron that is to be used as an alternative feed material in steelmaking as a replacement of scrap steel. Chalcopyrite is semi-conductive material therefore to optimize analysis by SEM it is made to be fully conductive by a incorporating a carbon coat into the powder to be analyzed.

2. Materials and methods

2.1. *Crushing and powder preparation*

In this context a detail description of necessary steps that were taken prior SEM and XRD characterization of the sample is clearly outlined and discussed. In most cases XRD can work with different variety of materials and is suitable for powders which comprises of numerous domains that are monocrystalline with different orientations and also with diffraction patterns that are incoherent. Therefore for a material to meet those requirements for XRD analysis with a finite beam the need for size reduction is essential. In this investigation the sample of chalcopyrite from Botswana was crushed as the 1st stage of comminution to obtain required particle size. The sample was subjected to compression crushing which is a technique usually applied to hard and abrasive rocks. A crystal of chalcopyrite is placed in a hard and wear resistant metal container and pounded with a rod of the same properties to the container. All the equipment used is thoroughly cleaned with toluene solvent and dried with tissue papers to avoid contamination as much as possible. Upon pounding the sample is crushed to particles of about 0.1 mm. In commercial practices, the crushers such as Jaw, Cone, impact breaker and hammer mill etc. are utilized to obtain required particle sizes.

The reduced particles of chalcopyrite are then pulverized using a PBM-V-4L-A Nano Powder Grinding Planetary Ball Mill Machine hence obtaining a powder of CuFeS_2 with granules size of about 0.1 μm . The ball machine uses impact and friction as its size reduction principle. In this operation it is also important to clean the mill jar and the balls with a toluene solvent and dried out with tissue papers to avoid contamination. The mill jar is filled with 15 mills balls of about 30 mm diameter (the higher the number of the balls the quicker the time to obtain the desired powder). The ball to powder ratio was about 4 magnitude. The powder is filled onto the remaining spaces. The ball mill machine is the run for 15 minutes at 300 rpm hence obtaining about 0.1 μm of chalcopyrite sample which can be used for X-ray and Scanning electron microscopy analysis.

2.2. *Mineralogical analysis (XRD & SEM/EDX)*

A bulk pulverized powder is place on an aluminum stud and analyzed using a General-Purpose X-ray diffractometers DRON-8. XRD basically enumerates the nature of crystallinity in a material. This is conducted to obtain peaks that are then used to obtain the parameters of relative planes (hkl) that are used to determine the structure of chalcopyrite. A trial test is ran at atleast a minute to obtain a range in which peaks form then an actual test is done at a 2θ range of 5° to 90° with operating conditions of Cu K alpha radiation, wavelength $\lambda = 1.54060 \text{ \AA}$ hence obtaining Intensity peaks at different 2θ values.

The chalcopyrite specimen powder is semi-conductive therefore prior to SEM analysis it is coated with a carbon coat. The carbon coat applied does not only induce a conduction path but also increases the secondary electrons to be detected for surface analysis and minimizes the heat buildup (charging) during imaging hence reduce chances of the beam being damaged. The analysis was done at 20.0 kV (Beam energy) and a magnification of X200 hence obtaining an SEM image at 100 μm and chemical analysis matched by the coupled EDX analyser.

3. Results and discussions

3.1. *XRD analysis*

Debugging software used with XRD on a an unprocessed and unseparated sample of chalcopyrite. This was done to see what other elements or minerals that occurs alongside or around the mineral of interest (chalcopyrite). As expected infinitesimal quantities of gangue materials such as calcite, Khamrabaevite, clinocllore, quartz and Yoshiokaite where observed. Chalcopyrite was the most abundant. The presence of small quantities of quartz might be due to contamination during collection of the sample. Defractographs of XRD in Fig. 1 shows sharp peaks of chalcopyrite which suggests that it has a good crystalline structure. Augmentation of peaks is in consistent with the small particle size of the powder. Match3 software is used on chalcopyrite peaks to determine its crystal lattice

structure. Match3 assigned diffraction peaks certain crystallographic planes (hkl) such as (1 0 1), (1 1 2), (1 0 3), (2 0 0), (0 0 4), (2 1 1), (2 1 3), (2 2 0), (2 0 4), (3 0 1) at 2 theta of 18.8° , 29.4° , 30.8° , 33.9° , 34.4° , 39.0° , 46.4° , 48.7° , 49.0° , 52.6° respectively etc. Match3 uses these hkl values together with the obtained $a=b=5.229 \text{ \AA}$ and $c=10.422$ values to automatically determine the crystal orientation of the chalcopryrite using Bragg's law.

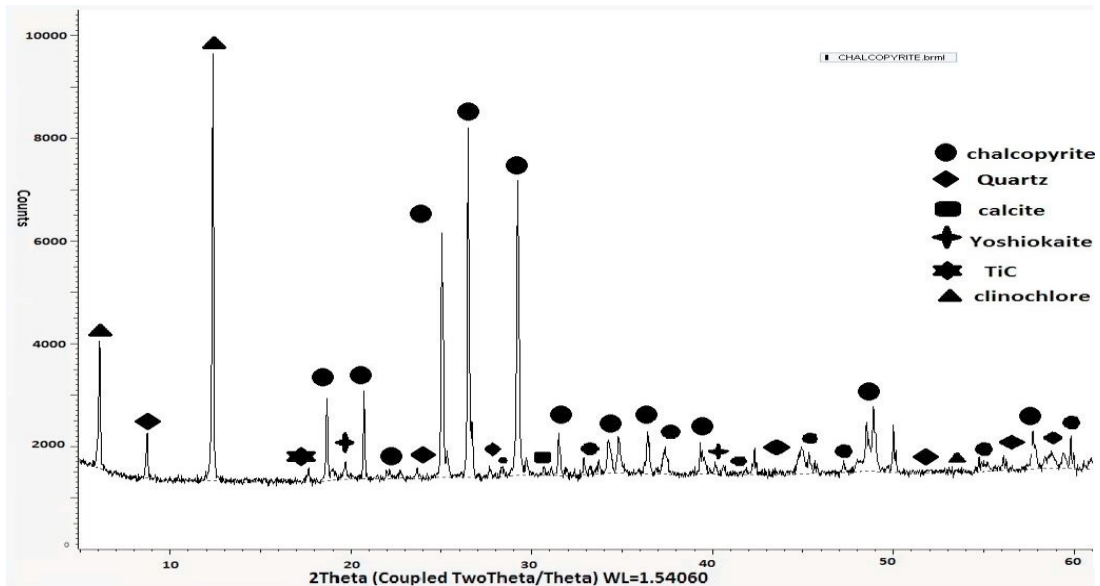


Fig. 1. Powder XRD patterns of chalcopryrite.

In this case the crystal structure was found to be a tetragonal configuration with $I-42d(122)$ as its space group. The structure corresponds with most literature and a and c values are close to nearly the same.

3.2. SEM/EDX Analysis

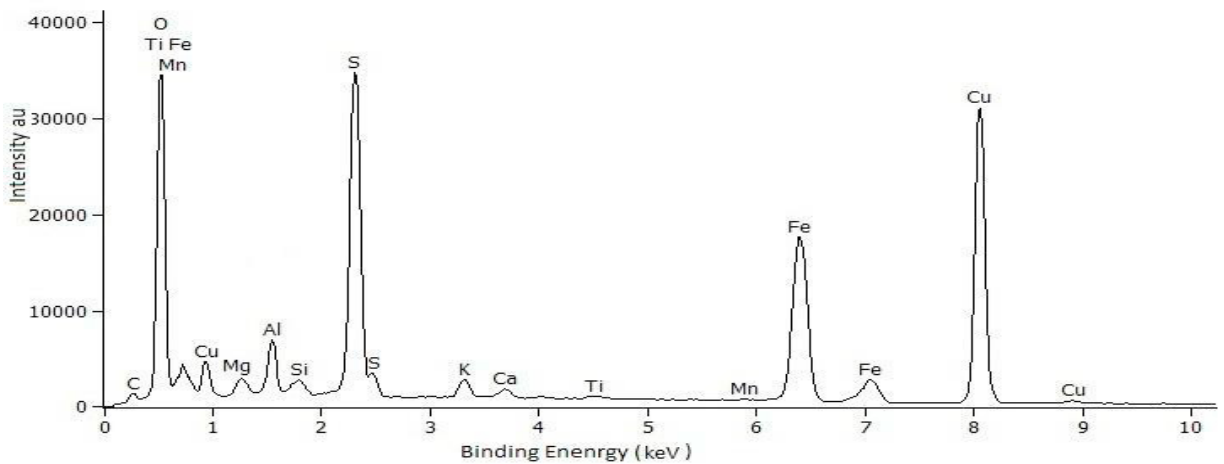


Fig. 2. EDX graph showing patterns/peaks of elements occurring in chalcopryrite.

Figure 2 above shows EDX graph analysis for the chalcopryrite powder. The elements recorded are Fe, S and Cu with the highest peaks. Fe has binding energies of around 0.5, 6.4, and 7.1 Kev. S is the most abundant. Majority of

other occurring elements such as Mg, Mn, C, Ti etc. had small peaks recorded. Ti, Mn and Oxygen also seem to exist with Fe. The powder was exposed to oxygen prior to analysis hence oxygen occurs alongside Fe as a result of oxidation.

Figure. 3.A. Shows the SEM image of the chalcopryrite scanned powder. The powder had equal microparticles but the particles shows different shapes which corresponds to different elements as supported by SEM images in fig. 3.a-c showing element map distribution of chalcopryrite. The powder Even though the powder was made to be conductive clear SEM imaging could not be obtained at resolutions more than X220 the powder was charging because of accrual of static electric fields meaning the presence of an oxide layer/film is a possibility. Also this means an image at a nanoscale could not be observed in this study. Agglomeration can be seen at boundaries of some particles shapes which indicate connectivity of such grains. The agglomeration would have been clear at a nanoscale level.

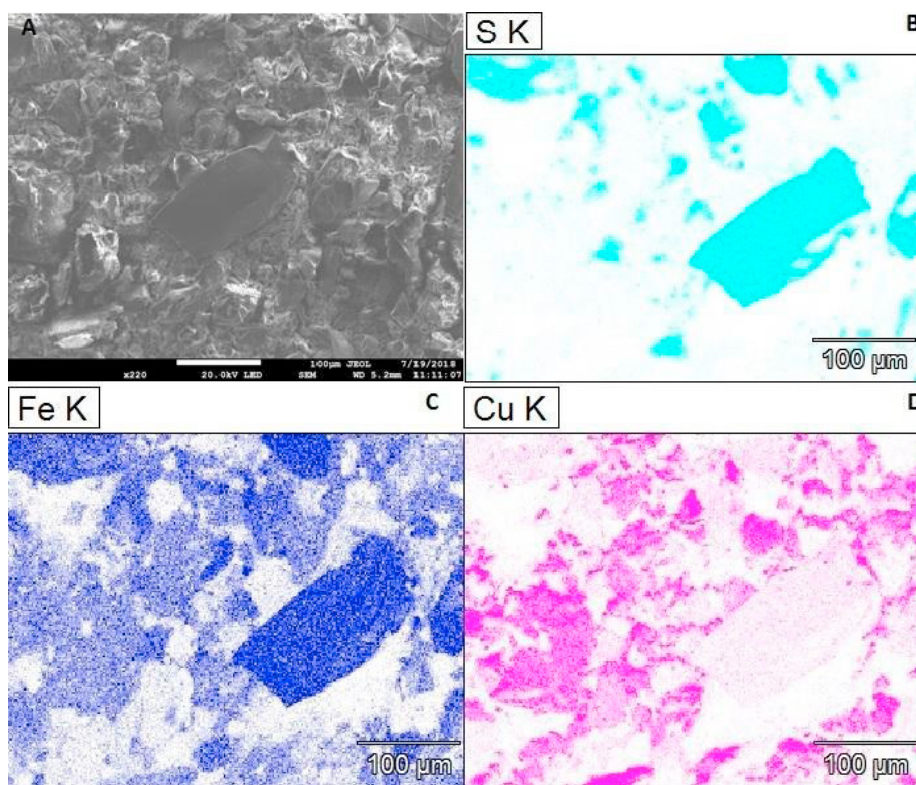


Fig. 3. (A) SEM image showing the morphology (B,C,D) element distribution of chalcopryrite (Cu, Fe & S₂).

Table 1. Of EDX chemical analysis confirms the appearance of Cu, Fe and S occurring as elements with high wt.% of 31.02, 33.07 and 34.08 respectively. This result of Cu, Fe and S being the highest in wt% had been in accordance with previous studies [1]. Other elements recorded an average of about 0.2 wt% and are considered as gangue/ impurities existing with chalcopryrite.

Table 1. SEM/ EDX (Energy dispersive X-ray) chemical analysis.

Element	Weight %	Atom %	Formula
C K	0.14	0.53	C
O K	0.12	0.34	O
Mg K	0.11	0.2	Mg
Al K	1.12	1.93	Al
Si K	0.16	0.26	Si
S K	34.08	47.88	S
K K	0.09	0.10	K
Ca K	0.04	0.04	Ca
Ti K	0.03	0.03	Ti
Mn K	0.02	0.02	Mn
Fe K	33.07	26.68	Fe
Cu K	31.02	21.99	Cu
Total	100.00	100.00	

Conclusions

In Summary XRD has revealed chalcopyrite to be surrounded by a region with contents of quartz, clinochlore calcite, TiC, and Yoshiokaitdan. SEM analysis have shown that the mineral chalcopyrite is rich in Fe, Cu and S with wt% values over 30 while majority of other elements averaged at less than 0.2 wt%. The chalcopyrite microparticles structure is tetragonal crystal lattice as determined by XRD characterization. High contents of Iron and Copper means both of the elements can be extracted simultaneously using relevant techniques for economic utilization. Occurrence of other elements such as C, Mn, Tin etc. are so low hence they won't cause any negative effect during the common practice of pyrometallurgy and leaching (hydrometallurgy of chalcopyrite) of chalcopyrite.

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