Investigation of mineral deportment in a copper ore from Botswana

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Abstract. Understanding the characteristics of minerals is key in developing effective techniques for copper ore processing to maximise recovery hence income. Most studies have focused on understanding the fundamentals and principles of dissolution kinetics, oxidation and leaching of copper minerals. New developments and technologies have made it possible to reveal that copper ores are fascinating and complex minerals. Other research concentrates on chemical and mineralogical analysis, hence revealing information such as properties, compositional change and analysis. In this paper X-Ray Diffraction (XRD) and Quantitative Evaluation of Minerals Scanning Electron Microscopy (QEMSCAN) are used as tools in quantifying chemical and mineralogical attributes of a copper ore (chalcopyrite bearing mineral) from Botswana as the objective. Obtained information was not limited to grain size and distribution, mineral associations and liberations characteristics of economic minerals in the ore and quantitative information being the latter. XRF indicates that the copper ore contains phases such as Al2O3, CaO, MgO, TiO2, V2O5 and SiO2, which is the dominant mineral with 60.6 wt% as well as traces of elements Fe, S, Pb, and Co with wt% of <0.02. Scanning Electron Microscope (SEM) peaks also confirmed these elements to exist in the mineral. Quantitative X-Ray Diffraction (QXRD) analysis entailed phases present with silicates being the dominant phases and their existence on the mineral by wt%. SEM peaks showed evidence of Fe, Si, Cu, S etc. which is consistent with XRF data. In addition QESCAN also revealed grain size of cuprite particles to be greater than 45 μm with < 0.24 % liberated. The copper ore is characterized with a possibility of extracting metals or elements of economic value.

1. Introduction

China has been the largest market for most of the world’s copper consuming nearly 40% annually. The reduced demand of copper from china that started in the year 2011 has caused a decline in the price of copper worldwide [1]. This circumstance has led to most mines to operate under strict financial and environmental regulations, using careful processing techniques that are less costly. This measures are incorporated to generate better income hence compensating for the declining market. Like most minerals, understanding copper ores through characterization is detrimental in development of efficient processing routes. A throng of copper sulphides such as chalcopyrite, chalcocite and covalite are slowly replacing bornite as a copper ore due to gradually decreasing grade [8]. This has created a problem for plant operators as they are facing a task to comprehend which minerals contribute to the grade since individual minerals are likely to behave uniquely during mineral processes such as comminution and beneficiation. Minerals which are likely or goes misidentified during processing may inhibit recovery of minerals of interest or increase processing costs. Many mining operations today face recovery problems due to insufficient data on ore properties from
characterization [2, 3]. Mineralogical data generation in the physical metallurgy (characterization) stage is an operation that has recently been adopted by most processing plants for copper ores and most minerals [4]. Copper ores as complex minerals usually contains pyrite, sulphides, zinc nickel non-metallic gangue such as quartz, feldspar and trace elements such as Te and Re etc. [16]. The copper ore (Chalcocite-bearing mineral) in question was obtained from Khoemacau mine near Maun, Botswana. Khoemacau is one of the copper mines affected by the world’s declining of copper prices which adds to a list in Botswana. According to Haest et al, 2011 chalcocite usually appears on 3 stage veins which are high angle veins, underdeveloped and associated haloes as a dark grey to black mineral, it has the formula Cu₂S. It is a secondary sulphide formed by alteration of other minerals such as copper leached away from near-surface sulphides. Its formation through atom by atom replacement makes it a pseudomorph mineral [10, 12]. Its formation from chalcopyrite (CuFeS₂) is explained as a reduction mechanisms of water table conditions due to oxygen attack. Lessening of such conditions favours the dissolution of Cu hence Cu displaces Iron in the iron sulphide to form Cu₂S [6]. Previous microscopy analysis on chalcocite indicated that the crystal system of chalcocite is orthorhombic in its natural state and at temperatures below 105°C, however it exhibits a hexagonal configuration at temperatures above 105°C [11]. Chalcocite is processed through hydrometallurgy and pyrometallurgy beneficiation techniques.

Effective parameters for processing can be established to optimize recovery of valuable minerals from chalcocite at reduced processing costs after a comprehensive mineralogical and chemical deportment is closely studied [2]. The objective of this research is to study the deportment of a copper ore hence revealing useful information such as chemical and mineralogical attributes and how they affect processing routes and steps. Techniques used to obtain such information include QEMSCAN and XRD. XRD coupled with quantitative analysis by QEMSCAN (based on SEM and equipped with XRF) facilitates much improved ore control hence recoveries are optimized. QEMSCAN is a recent technology based on scanning electron microscopy (SEM). XRF of QEMSCAN determines the compositional analysis of minerals while XRD provides crystalline phases existing in in the ore [14]. A recent research by Gitari et al, 2017 studies focused on XRD and XRF physicochemical and mineralogical characterization of a copper ore to reveal major and trace species present. In this context, knowledge on chemistry and mineralogical nature of the copper ore such as liberations and associations, grain size distribution, constituents and phase composition etc. it is possible to suggest a processing route since this factors affect recovery rates.

2. Materials and methods

2.1. Sample preparation

A sample of CuS (as shown in Figure 1.) was collected from Khoemacau mine and sent to SGS South Africa for QEMSCAN and XRD analysis. It was crushed to a powder with granules of 1 mm particle sizes and the powder split into 2 for further experimental analysis. 10-15 g was split out to make 900 blocks to be examined by QEMSCAN and about 50g of the other split was pulverized for XRD analysis.

![Figure 1. Sample of chalcocite from khoemacau mine.](image-url)
These steps are summarized in figure 3. The blocks prepared for surface analysis by QEMSCAN were cut at transverse angle in the manner shown in figure 2.

2.2. Mineralogical analysis (QEMSCAN)
QEMSCAN 650 (Quantitative Evaluation of Minerals SEM) is a technology based on secondary electron microscopy (SEM). It is an auto modified SEM, it has four light–element Dispersive X-ray Spectrometers (EDS) and provides quantitative and reliable data as compared to the traditional optical microscopes. QEMSCAN specific mineral search (SMS) was used to provide details of Cu speciation and elemental deportation, grain size distribution as well as liberations and associations, quantitative analysis of major elements and grain size distribution [18]. X-ray diffraction (XRD) analysis an inexpensive technique that quantifies ores to obtain phases present in the ore. Co-radiation has recently replaced the use of Cu-radiation in XRD characterization of copper ores. Copper ores are likely to contain elements such as Fe, Cr, Co and Mn that can cause X-ray fluorescence hence background scattering often associated with the use of cu-radiation [17]. XRF data of QEMSCAN was then validated with results from XRD.

2.3. Chemical analysis (X-Ray Fluorescence Spectroscopy XRF)
XRF borate fusion and ICP sodium peroxide fusion (Including Ag) was used to conduct the chemical analysis of the copper ore, most base metals are analysed by XRF. It can detect trace elements
Occurring at sub ppm levels, Enzweiler et al (1996). It was used to detect major and trace oxides together with their respective proportions.

3. Results and discussions

3.1. Chemical analysis

XRF Analysis XRF elemental analysis results are shown in table 1.0. The results shows minerals of economic value, routine oxides as well as gangue materials. The ore sample consisted of mostly quartz as a gangue material which recorded a high wt. % (60.6). Even on visual examination of the sample evidence of quartz could be seen on the surface of the mineral samples collected. Most of land in Botswana is covered with SiO$_2$ hence the high amount of quartz occurring alongside mineral of interest. SiO$_2$ is have very low solubility in solutions hence remains as a impurity solid. The abundance of quartz in the ore contributes to the overall hardness of chalcocite hence milling time for this ore will be increased during processing [16]. The presence of CaO is known to occur the ore due to calcium leaching by solution and consequent reprecipitation [13]. The sample also contained high Al$_2$O$_3$ which is likely to be present in mica and significant amounts of Cu, Fe, K$_2$O and minor quantities of TiO$_2$, V$_2$O$_5$ as well as affinity of Cr etc.

According to Kotoky et a Mn present in mineral samples may indicates a warm and humid environment in which the ore exist. This correlates with climate in botswana which is warm/hot and humid. Quantities of Cu and S present in the sample are not related to chalcopyrite and exists in the form of Cu$_2$S (chalcocite). All the lower limit of detection (LLD) for all the phases fall in the range 0.01-0.05 %.

| Element  | Cu Ore % | Ldetection % | Udetection % |
|----------|----------|---------------|--------------|
| Al$_2$O$_3$ | 13.7    | 0.05          | 100          |
| CaO      | 4.4      | 0.01          | 100          |
| Co       | <0.02    | 0.02          | 100          |
| Cr       | <0.05    | 0.05          | 100          |
| Cu       | 1.09     | 0.05          | 100          |
| Fe       | 2.74     | 0.05          | 100          |
| K$_2$O   | 3.82     | 0.01          | 100          |
| MgO      | 2.83     | 0.05          | 100          |
| Mn       | 0.17     | 0.05          | 100          |
| Na$_2$O  | 1.62     | 0.05          | 100          |
| Ni       | 0.06     | 0.05          | 100          |
| P$_2$O$_5$ | 0.164  | 0.01          | 100          |
| Pb       | <0.05    | 0.05          | 100          |
| S        | 0.18     | 0.01          | 100          |
| SiO$_2$  | 60.6     | 0.05          | 100          |
| TiO$_2$  | 0.64     | 0.01          | 100          |
| V$_2$P$_5$ | 0.02    | 0.01          | 100          |
| Zn       | <0.05    | 0.05          | 100          |

3.2. Mineralogical analysis

SEM analysis In this subsection phase distributions in the ore are analysed. SEM imaging shown in the following figure shows that a large spot A the sample scanned is composed of Cu and S likely occurring in the form of Cu$_2$S. This is proved by SEM Cu peaks at ~0.9 KeV and ~8.08 KeV which shows copper dominating the spot with ~41% above S with ~19%. Spot B which is a little darker than A represent Fe (~40%) as shown by the second Peak mapping. Other analysis on different spots are shown in appendix section.
Figure 4. SEM images showing minerals detected in the copper ore.

3.2.1 XRD

Table 2.0 XRD crystalline phases of minerals and their abundance in %.

| Mineral       | Approx Formula | Approximate Abundance % |
|---------------|----------------|-------------------------|
| Quartz        | SiO₂           | 28.40                   |
| Mica          | KAl₂Si₃O₈(OH,F)₄ | 18.35                   |
| Plagioclase   | NaAlSi₃O₈ - CaAl₂Si₂O₈ | 25.62                   |
| Chlorite      | (Mg,Fe)₃(Si,Al)₄O₁₀(OH)₈ | 19.30                   |
| K-feldspar    | KAlSi₃O₈         | trace                   |
|               | Total Silicates | ~ 92.48                 |
| Calcite       | CaCO₃           | 7.52                    |
|               | Total Carbonates | ~ 7.52                 |
| Cuprite       | Cu₂O           | trace                   |
| Chalcopyrite  | CuFeS₂          | trace                   |
| Covellite     | CuS            | trace                   |
|               | Total Cu oxide/sulphide | trace             |

Table 2.0 shows crystalline phases that occurs within the sample as detected by quantitative X-ray diffractometer (QXRD). XRD peaks of these respective phases are shown in figure 5.

The results obtained from QXRD indicated that the copper ore investigated consisted of mostly silicates followed by carbonates at % of 91 and 8 respectively. The rest was negligible amount of copper oxides/ sulphides traces in the form of cuprite, chalcopyrite and covellite. Quartz was the most abundant silicate as a gangue material with 28.40 abundance %. This results are consistent with XRF results analysed. The peaks in the next figure shows quartz recorded the highest peaks and the sharp peaks represents the material being brittle.
3.2.2 QEMSCAN this results of mineral phases detected by QEMSCAN are also consistent with data detected by XRD where silicates occurrences dominates in the sample. In addition to these minerals. Other included minerals, listed in Table 3.0 below, were found occurring in trace amounts. The grain size distribution (GSD) analysis in Figure 6 shows the sample has fine to coarse size fractions

| Mineral  | Approx Formula | Approximate Abundance % |
|----------|----------------|-------------------------|
| Silicates| -(SiO$_4$)$_n$ | 91.78                   |
| Calcite  | CaCO$_3$       | 4.96                    |
| Other    | -              | 0.71                    |
| Cc/Cov   | Cu$_x$S$_y$    | 1.68                    |
| Cuprite  | Cu$_2$O        | 0.57                    |
| Other    | -[O$_2$-]      | 0.3                     |
| Oxides   | Total          | 100                     |
80% of Cc/Cov is greater than 45 μm grain size range, while 70% of the cuprite is greater than 45 μm grain size. QEMSCAN takes advantage of point counting technique in order to determine the degree of liberation of the copper ore. The grains of copper minerals were counted as well as gangue materials locked into the ore and the relative percentages are given in table 4.0. Figure 7 (below) indicates that ~28% of Cc/Cov and ~49% of cuprite is fully liberated. If particles are liberated it means more than 80 % of the particle is the mineral of interest. Liberation can dictate recovery rate of minerals. Poor liberation rates leads to lower recovery of coarse particles [9] therefore for efficient recovery of minerals of interest from gangue the ore must be adequately liberated. However in real practices a 100 % liberation is not possible hence particles with locked gangue and minerals of interest are produced (Sutherland et al). Locked particles are those that contains more than one interface between phases (Fuso, 2015). Locked particles also have less than 30% of particles being the mineral of interest. In High (Hi) Middlings 50-80% of particle is the mineral of interest as compared to Lo Middling with 30-50 being the mineral of interest.
The rest of the Cc/Cov and cuprite minerals, which are classified as Hi Midd, Lo Midd and Locked, are associated with other minerals present in the sample. The associations, are shown in Table 4.0. The associations are summarized by pie chart shown in Fig 8 which reveals that 70% of the total Cu in the total sample occurs as Cc/Cov, and 26% in the cuprite. Chalcocite liberation with cuprites is fairly good hence the reason for low association values.

![Figure 8. Distribution of total Cu in different phases.](image)

**Table 4.0 liberation and associations of Cc/Cov**

| Liberation and Association of Cc/Cov | %     |
|-------------------------------------|-------|
| Liberated Cc/Cov                   | 27.41 |
| Cc/Cov, Associated with Cuprite    | 6.09  |
| Cc/Cov, Associated with Silicates  | 38.61 |
| Cc/Cov, Associated with Calcite    | 3.05  |
| Cc/Cov, Associated with Oxides     | 0.12  |
| Complex (Cc/Cov and more than two other minerals) | 27.73 |
| Other (Associations without Cc/Cov) | 0.00  |

**Conclusions**

1. QXRD data showed that the Cu ore sample is mostly comprised ~91% silicates, ~8% carbonates and trace amounts (<1%) of Cu oxide/sulphide were recorded. Quartz being the most dominant as a gangue material.
2. SEM images shows a fine dissemination of element Cu throughout the sample.
3. The XRF and XRD characterization showed no substantial variations in chemical analysis of major occurring elements. However a slight deviation in other trace elements is observed.
4. Cc/Cov and cuprite are the only two Cu-bearing minerals detected by QEMSCAN analysis. ~28% of the Cc/Cov and ~49% of the cuprite was found to be liberated. 70% of the Cu in the total sample occurs in the Cc/Cov group, and 26% in the cuprite. The ore consists predominantly quartz which increases hardness, it is suggested that this ore be milled to 80% <106m and subjected to
flotation by initially adding a sulphidizing reagent (to sulphidise the cuprite) and then perform sulphide flotation.

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Appendix

SEM images showing minerals detected in the copper ore A,B,C

A

B
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