



A Review of the Flotation of Copper Minerals

Tinashe O. Ndoro^{a*}, Lordwell K. Witika^b

^a*Department of Metallurgical Engineering, University of Zimbabwe, Box MP167 Harare, Zimbabwe.*

^b*Department of Mineral Processing and Metallurgy, University of Zambia, Lusaka, Zambia.*

^a*Email: tnoswald@gmail.com*

^b*Email: lwitika@unza.zm*

Abstract

Copper is most commonly present in the earth's crust as copper-iron-sulphide and copper sulphide minerals, for example, chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4) and chalcocite (Cu_2S). Copper also occurs to a lesser extent in oxidised minerals, for instance, malachite ($\text{Cu}_2(\text{OH})\text{CO}_3$), azurite ($\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$) and chrysocolla ($\text{CuO}\cdot\text{SiO}_2$). These oxidised copper minerals are found in weathered regions of most copper sulphide ore bodies. The overlying oxidic ore is usually stockpiled after it is removed from the sulphide lode and left unprocessed as the sulphide ore is simpler to recover by conventional flotation procedures and thus, more attractive to the plant operator. Oxidic ore can be concentrated using flotation or, if it has a low acid demand, it may be economic to acid heap leach the stockpile. The recovery of these copper minerals by flotation or hydrometallurgy from ores, typically containing 0.5%TCu (open pit mines) and 1-2%TCu (underground mines) is of great commercial importance. This paper reviews the literature on the recovery of the above mentioned minerals by flotation. The increasing complexity of ore deposits, declining ore grades and higher global demand for copper has resulted in increased ore processing by flotation plants around the world. The depletion of high-grade ores, increased demand for metals and separation difficulties associated with low-grade or refractory ores, has resulted in new flotation challenges in terms of economic and sustainable beneficiation of these ores. However, improvements in technology have allowed various processing plants to treat low-grade ores at almost no extra cost.

* Corresponding author.

This has allowed companies to sustain their mining operations and the livelihood of the mining community. Therefore, in order to appreciate the challenges and innovations in terms of recoveries and concentrate grades due to the exploitation of complex and low-grade ores, it is important to present this literature review by first highlighting the fundamental principles of flotation. These principles generally involve the chemical and electrochemical aspects considered in flotation, which include the use of various reagents namely, collectors, frothers and modifiers such as activators and depressants. Flotation of sulphidic and oxidic copper minerals is reviewed, with particular reference to previous studies of refractory copper ore flotation.

Keywords: Flotation; recovery; refractory.

1. Introduction

Froth flotation is defined as a physico-chemical process which exploits the differences in the electrochemical properties of mineral surfaces, that is, between hydrophobic and hydrophilic surfaces, which either occur naturally or artificially induced by chemical reagents [1, 2]. Figure 1 shows the principle of froth flotation.

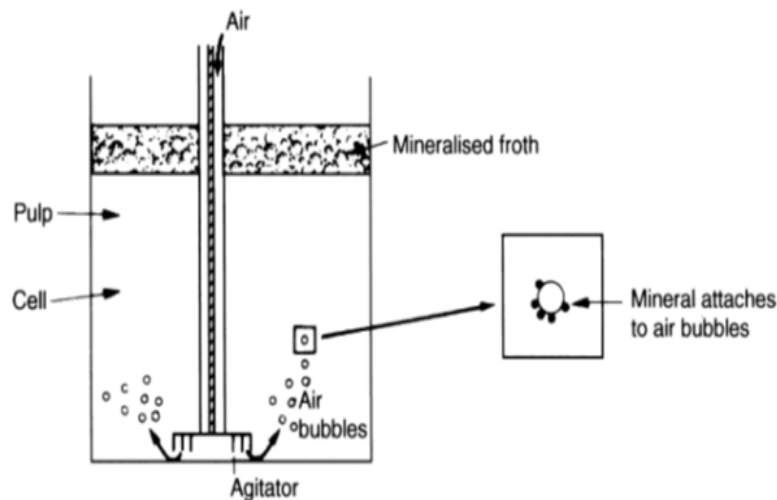


Figure 1: Principle of flotation [3].

Froth flotation can be regarded as a system [3], with various sub-processes and interactions. For flotation to take place an air bubble must be able to attach itself to a particle in the mineral suspension known as flotation pulp. For this to happen, the particle should be small enough to adhere and be carried by the bubble to the surface into the froth layer, otherwise the particle will drop off the bubble, when the bubble starts to rise. As such, froth flotation is mainly used in the separation of fine particles.

Therefore, froth flotation pulps consist of mixtures of solid particles in an aqueous solution, with small additions of surface active agents and air bubbles. The active agents are either inorganic or organic reagents. Hence in any flotation pulp all three phases, solid, liquid and gaseous are present. The properties of the bulk phases influence and determine the characteristics of the interfaces formed between the adjoining phases. Solid, liquid and gas are the three main phases involved in the flotation interactions.

In the three-phase system created, three interfacial tensions are present as shown in Figure 2: the solid-air (γ_{sa}) tension, solid-liquid (γ_{sl}) tension and liquid-air (γ_{la}) tension. These interfacial tensions develop an angle between the mineral surface and the bubble surface.

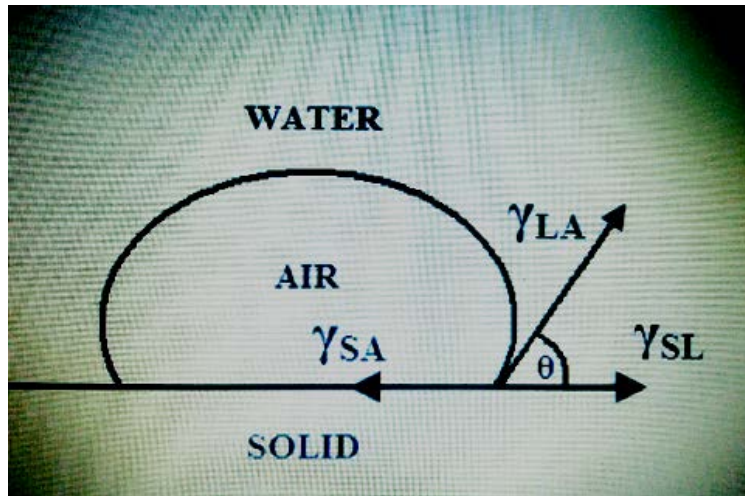


Figure 2: Contact angle between bubble and particle in an aqueous medium [5].

At equilibrium these forces give a relationship frequently referred to as the Young’s modulus equation;

$$\cos \theta = \frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}} \dots\dots\dots (1)$$

where, γ_{sa} , γ_{sl} and γ_{la} are the surface tensions between solid-gas, solid-liquid and liquid-gas respectively and θ is the contact angle between the mineral surface and the bubble.

On the other hand, the force required to break the particle-bubble interface, called the work of adhesion, is equal to the work required to separate the solid-gas interface and to produce separate gas-liquid and solid-liquid interfaces was derived by Dupre as;

$$W_{sa} = \gamma_{la} + \gamma_{sl} - \gamma_{sa} \dots\dots\dots (2)$$

Combining equations 1 and 2 gives;

$$W_{sa} = \gamma_{la}(1 - \cos \theta) \dots\dots\dots (3)$$

From equation 3 it can be seen that the hydrophobicity of a mineral increases with the contact angle; minerals with a high contact angle are said to be aerophilic, that is, they have a higher affinity for air than for water [3].

Successful industrial practice of flotation [4] involves knowledge and optimisation of four important components of flotation process, namely:

- i. Mineralogical characteristics of the ore (mineral association, liberation size, presence of slime particles

and soluble species contributed by the ore).

- ii. Surface colloid and reagent chemistry which determines selectivity of separation (collectors, frothers, activators, depressant, modifiers and dispersant).
- iii. Process engineering (feed preparation (size reduction), cell design and control system).
- iv. Operating parameters such as aeration rate, temperature, Eh/pH, ionic strength and flotation circuit configuration.

Also according to [6] overall separation efficiency in flotation is dependent on:

- i. Surface chemistry factors such as bubble attachment, mineral reagent interactions and reagent chemistry. These factors are related to equilibrium considerations contributing selectively to separation.
- ii. Hydrodynamics factors which contribute to the kinetics of flotation such as agitation, air flow rate, dispersion and cell design control recovery of minerals.

In the flotation process a number of physico-chemical variables are important. According to [6], the important physico-chemical variables in flotation are:

- i. Role of mineral/water interface.
- ii. Surface charge on the minerals.
- iii. Effect of hydrocarbon length of the collector.
- iv. Effect of neutral molecules.
- v. Role of polar functional group of the collector.
- vi. Role of solution chemistry of the collector.
- vii. Role of inorganic ions (activator and depressant).
- viii. Effect of temperature.
- ix. Ore properties such as grade, mineralogy, degree of oxidation and liberation of minerals.

2. Flotation Reagents

Reagents are the most important part of the flotation process [7]. The selection of reagents is of great importance for the process to give the most effective separation and concentration results. Thus, in commercial plants, the control of reagent additions is the most important part of the flotation process. Flotation reagents can be categorised into three main classes, on the basis of the function of a particular reagent. They are divided into collectors, frothers and modifiers.

2.1. Collectors

Collectors are basically organic chemical compounds, which differ in chemical composition and function. The basic purpose of the collector is to selectively form a hydrophobic layer on a given mineral surface in the flotation pulp and thus provide conditions for attachment of the hydrophobic particles to air bubbles and recovery of such particles in the froth product. Collectors can be divided into distinct groups according to their ability to dissociate in water. Figure 3 shows the classification of collectors.

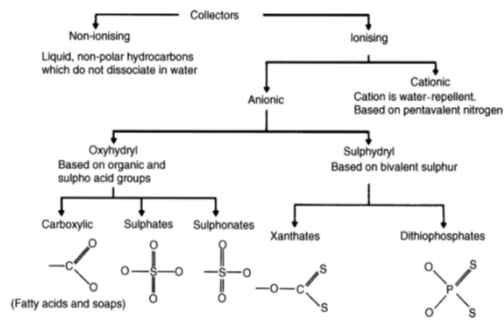


Figure 3: Classification of collectors [3].

2.2. Frothers

Frothers are heteropolar surface-active compounds that lower the surface tension of water and have the ability to adsorb on the air bubble–water interface. Their presence in the liquid phase increases the film strength of the air bubbles, thus providing better attachment of hydrophobic particles to the bubbles. The heteropolar structure of the frother makes the non-polar group to orientate towards air and the polar group towards water as shown in Figure 4.

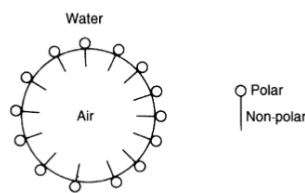


Figure 4: Action of Frother [3].

A good frother should have no collecting power but should be able to ensure that the floated minerals are transferred from the float cell to a collecting launder [8]. Frothers must be to some extent soluble in water so that they are evenly distributed in an aqueous solution, to ensure that their surface active properties are effective [3]. The effectiveness of frothers is dependent on their composition and Figure 5 shows the respective groups.

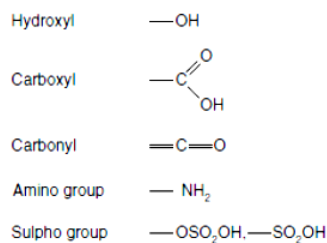


Figure 5: Functional groups in effective frothers [3].

The most widely used frothers include natural chemicals such as pine oil, cresylic acid, and synthetic reagents such as methyl isobutyl carbinol (MIBC) and polyglycol ethers [5]. However, alcohols (OH) are the most

commonly used, since they have no collector properties and in this respect are preferable to other frothers such as carboxyls, which are also powerful collectors.

2.3. Modifiers

Modifiers are chemicals used extensively in flotation to modify the action of the collector, making collector action more selective towards certain minerals [3; 7]. Modifiers can be classed as activators, depressants and pH modifiers. Activators react with the mineral surface so that they become hydrophobic due to the action of the collector, depressants increase the selectivity of flotation by rendering certain minerals hydrophilic and pH modifiers regulate the ionic composition by changing the ion concentration of the hydrogen ion in the pulp [7]. Table 1 shows some of the modifiers used in sulphide and non-sulphide mineral flotation.

Table 1: Modifiers used in sulphide and non-sulphide flotation [9].

Inorganic	Small organic	Polymeric molecules
Ammonium sulphide (sporadic)	Mercaptoethanol (sporadic)	Carboxymethylcellulose (CMC)
Ca, Mg, Al and Fe salts	Organic dyes (sporadic)	Dextrin
Copper sulphate	Polyamines (diethyleneamine [DETA], triethyleneamine [TETA])	Guar gum
Hydrofluoric acid	Sodium thioglycolate and its thiocarbonate derivative (sporadic)	Modified guar
Lead nitrate	Surfactants (mostly non-ionic and anionic; sporadic in sulphides, more regular in non-sulphide)	Lignin sulphonates
Lime	Tannics or quebracho (sporadic in sulphide, more regular in non-sulphide)	Polyacrylates
Phosphoric acid		Synthetic functionalised polymer
Potassium dichromate (sporadic)		
Soda ash		
Sodium and zinc cyanide		
Sodium ferro-cyanide (sporadic)		
Sodium fluoride		
Sodium hypochlorite		
Sodium meta and polyphosphates		
Sodium metasilicate		
Sodium sulphide and hydrosulphide		
Sodium sulphide and sulphur dioxide		
Sulphuric acid		
Zinc sulphate		

3. Flotation of Sulphide Ores

Sulphide ores are the major sources of base metals like Copper, Lead, Zinc, Nickel and Cobalt. Beneficiation of these base metal sulphide minerals is predominantly through the froth flotation technique.

Some of the most important sulphide minerals are: Galena (PbS), Sphalerite (ZnS), Chalcocite (Cu₂S), Covellite (CuS), Chalcopyrite (CuFeS₂), Pyrite (FeS₂) and Molybdenite (MoS). According to [4] distinguished features of these minerals are:

- i. The minerals are covalently bonded compounds and possess very low solubility; each of these minerals has a definite solubility product in water.
- ii. Sulphide minerals are meta-stable and are prone to surface oxidation in the presence of water and oxygen.
- iii. Minerals are electronic semi-conductors which can act as a source or sink for electrons and therefore can support electrode reaction at the surface.
- iv. Most of the sulphide minerals are regularly charged in working range of pH and therefore the electrical double layer interaction oppose the adsorption of commonly used anionic reagents.
- v. Some of the sulphides have feeble natural hydrophobicity. Some of these are capable of rapid and complete flotation in the absence of conventional collectors.
- vi. One of the important consequences of the electrochemical nature of the surface reaction is the galvanic interaction between the grinding media and the sulphide minerals.
- vii. Sulphide ore minerals are generally floated using thiol type reagent xanthates and dithio-phosphates. Oxidised minerals do not respond to these collectors and hence require surface modifying treatment.

Sulphide copper ores are considered easy to treat provided that the main copper mineral is chalcopyrite [7]. However, in case the ore contains secondary copper minerals, such as chalcocite, bornite and covellite, depression of pyrite may be a problem because the pyrite can be activated by copper ions generated during the grinding operation [7]. Some copper sulphide ores can be partially oxidized, also influencing the selection of a reagent scheme. Copper sulphide ores are normally finer grained than porphyry copper ores and require finer grinding (i.e. 70–80% <200 mesh) [7].

3.1. Reagents Used In the Flotation of Sulphide Ores

Commonly used reagents in industrial flotation plants are Collector, Frother, Activator, Depressants and pH modifiers. Of the above, collectors are the most important reagents which play a critical role in sulphide flotation. Sulphydryl or thiol type collectors which in general consist of the “SH” group in combination with an organic radical have extensive application

Extensive research has been carried out to understand surface chemistry and interaction between collectors and sulphides. Some of the important aspects as listed by [4] are:

- i. Interaction between sulphide minerals and thiol collectors takes place by a corrosion type mixed

potential mechanism involving simultaneous electrochemical reactions at mineral water interface.

- ii. Potential difference of the mineral solution interface is the most important parameter determining the rates of reactions causing flotation which is termed as Redox Potential (Eh). By monitoring oxidation/reduction environment of the pulp, Eh can be controlled and can be used as one of the on-line control parameters of flotation process in the plant for naturally or weakly floatable sulphide minerals.
- iii. In order to enhance the selectivity of collection, many modifying agents like activators and depressors are used for soluble sulphide minerals.

However, it has been reported that flotation kinetics/selectivity of many soluble sulphides, for example, sphalerite and pyrrhotite requires activation under normal flotation conditions. Longer chained xanthates are generally used for improving selectivity [5] and research work has confirmed a relationship between carbon number, flotation response and solubility product of corresponding metal xanthates. Xanthate collectors are not capable of recovering ultra-fine particles (<10 μ m) and significant losses can occur in the fine fraction. They are not selective with respect to iron sulphide. The average consumption of xanthate is reported to be relatively very high, ranging from 50 to 150 g/MT [4]. Therefore, a mixture of two or three types of xanthates at different stages of collection also in combination with dithio-phosphates and certain nitril compounds are being used in many sulphide flotation plants.

The choice of collector also depends on the nature and occurrence of copper and associated sulfides. In most cases, xanthate collectors are used alone or in combination with dithiophosphates or thionocarbamates [7]. Dithiophosphates and thionocarbamates are normally used when secondary copper minerals are present in the ore or when the copper flotation is carried out at lower pH [7].

Another important parameter which has a remarkable effect on the flotation of sulphide minerals is pH. It is established that xanthates decompose in acidic environment and hence, resulting in lower flotation recovery [4]. Thus, through proper pulp pH control selective flotation of one sulphide from another can be achieved.

As regards to other reagents used in sulphide flotation, depressants like Sodium Cyanide, Zinc Sulphate and Sodium Meta bi-sulphide are common [4]. Cyanide has been used as a depressant and deactivator in the flotation of sulphide minerals [6]. However, the actual effect of cyanide in the flotation process is still not clear and depends greatly on solution chemical conditions and the reaction time. It has been reported that cyanide activates, rather than depresses flotation under some cases [12; 13]. The effectiveness of a depressant depends on the concentration and selection of collector(s) [4].

Pine oil, Methyl isobutyl carbinol (MIBC) and Cresylic acid are commercially used as frothers in sulphide flotation depending upon overall economics and nature of frother, whether brittle or hard, and froth bubble size required [6]. Frother choice varies from [7] one ore type to the other and most commonly, an alcohol-type frother is used. The exception is when clay slimes are present in the ore; then a mixture of two frothers or a glycol-type frother is employed.

If the sulphide is associated with oxides and oxide minerals, the ore is subjected to sulphidising by sodium

sulphide, followed by flotation with xanthate or metacaptobenzols and mecarptans [4]. The sulphidising process needs to be monitored carefully, generally done in stages and preferably through control of pulp Eh. Chelating agents and cationic collectors are also used for flotation of oxidised minerals [4].

4. Flotation of Oxidic Copper Minerals

Oxide copper minerals are an important copper resource [14; 15]. The oxide copper minerals are found in weathered regions of most copper sulphide ore bodies [14; 16]. The overlaying oxide ore is usually stockpiled after it is removed from the sulphide lode and left unprocessed as the sulphide ore is simpler to recover by conventional flotation procedures and thus, more attractive to the plant operator. Oxide ore can be concentrated using flotation or, if it has a low acid demand, it may be economic to acid heap leach the stockpile [14; 16; 17].

The concentration of oxidised copper minerals by flotation has been extensively studied [7;8]. It has been applied in Central Africa, especially Congo [9;10;11]. However, oxide copper minerals do not generally respond well to traditional concentration methods using known sulphide copper collectors. Marabini and his colleagues [21] noted that surface properties of copper oxide minerals are a significant factor in their problematic recovery. Barbaro and his colleagues [22] highlighted that copper oxide minerals are prone to dissolution, lack mechanical strength and possess strongly hydrophilic surfaces, which are difficult to transform into hydrophobic surfaces. Conventional sulphide copper collectors fail to adhere to the oxides, resulting in excessive collector consumption, limited selectivity and poor recovery [5]. Additionally, the mineral assemblage in oxidised copper zones contains gangue that also creates slimes, detrimental to recovery, grade and frothing conditions [23]. Thus, their recovery in a froth flotation circuit requires special treatment. The flotation process has two most common approaches:

- i. Fatty acid flotation of oxide copper minerals from siliceous ore [24; 14; 25; 16].
- ii. Sulphidisation of oxide minerals using sodium sulphide (Na_2S), sodium hydrosulphide (NaHS), or ammonium sulphide ($(\text{NH}_4)_2\text{S}$) followed by flotation using xanthate or other sulphide collectors [26; 27].

Most of earlier research on flotation of oxidised copper minerals was of empirical nature [8]. Although a number of methods have been proposed for flotation of these ores, only a few have advanced beyond the laboratory stage. However, flotation of most oxidised copper minerals is difficult.

One of the major problems with flotation of oxide copper minerals, at industrial scale is that the floatability from natural ores depends largely on the mineralogy of the ore and the gangue composition [7]. As such, the floatability of oxide copper minerals that are present in the ore containing carbonaceous and dolomitic gangue is significantly different from the flotation properties of oxide copper containing siliceous gangue minerals.

Direct flotation of ores containing carbonaceous and ferruginous gangue gives poor results because of the non-selectivity of collection. The presence of various types of clay in the ore has a significant effect on flotation properties of oxide minerals [8, 12]. According to [18] prior de-sliming may permit successful flotation of malachite and azurite ores. In some cases, treatment of the pulp with flocculants such as acrylic acid polymers

may be used as a substitute for the de-sliming step [7].

Long chain carboxylic collectors such as oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$) or their salts, in the pH range of 8 to 10.5, have been known to give good recovery of malachite and azurite but mediocre recovery of cuprite and tenorite [8].

It has also been reported that sulphhydryl compounds are also effective collectors for the carbonates of copper but excessive amounts of these reagents are required for good recoveries if used alone. Sulphidisation (using Na_2S , H_2S or molten sulphur) can reduce collector consumption. However, the amount of sulphidising agent is critical because a slight excess leads to lack of floatability [13]. Hence, stepwise sulphidisation is becoming the standard procedure [9, 11].

4.1. Oxidic Copper Ores

Of the 120 oxide-containing minerals identified mainly from the Central and South African regions, only a few have any economic value. Some of the most important copper oxide minerals [27] are listed in Table 2.

Table 2: Economically valuable copper minerals [27].

Mineral	Chemical formula	Copper content (%TCu)	Specific Gravity (SG)	Colour
Cuprite	Cu_2O	88.8	5.9	Brick red
Tenorite	CuO	80.0	6.5	Black
Malachite	$\text{Cu}_2(\text{OH})\text{CO}_3$	57.4	3.9	Green
Azurite	$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	55.3	3.7	Blue
Bronchantite	$\text{Cu}_4(\text{OH})_6\text{SO}_4$	56.6	3.9	Emerald green
Atacamite	$\text{Cu}_2(\text{OH})_2\text{Cl}$	44.6	3.8	Green, blue
Antlerite	$\text{Cu}_3(\text{OH})_2\text{SO}_4$	54.0	3.9	Emerald green
Chrysocolla	$\text{CuO} \cdot \text{SiO}_2$	10 – 36	2.2 – 4	Blue
Chaecantite	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	25.5	2.2	Deep blue

Most of the known oxide copper deposits with the minerals listed in Table 2 are located in the Republic of Congo (Katanga) and Zambia whereas only a few deposits are located in Chile, Peru, Canada and the United States. The most significant industrially beneficiated copper minerals among the oxide copper ores are Malachite and Azurite, whereas Chrysocolla and Cuprite are the less important [7, 14].

Usually, oxide copper ores contain more than one copper oxide mineral, and also contain mixtures of sulphide and oxide copper minerals. According to [27], the oxide copper ores can be divided into the following five groups:

- i. *Oxide copper ores* – ore is predominantly malachite with significant quantities of cobalt. The ores can

be further sub-divided into two main groups on the basis of mineral composition: (a) oxide ore that contains carbonaceous gangue minerals (carbonate, dolomite) with little or no silica; and (b) oxide ore, where silica is the predominant gangue mineral. The gangue composition of the ore plays a decisive role in selection of reagent scheme for the beneficiation of the ore. These ores also contain cobalt minerals, mainly carrolite (Co_2CuS_4) and cobaltite (CoAsS).

- ii. *Copper oxide mixed ore (Type 1)* – the main copper minerals found in these ores include malachite, pseudo-malachite, chrysocolla and some tenorite. Ores may also contain mainly siliceous gangue minerals, including sphero-cobaltite as the main cobalt minerals. The carbonaceous types also contain an appreciable amount of clay slime minerals.
- iii. *Copper oxide mixed ore (Type 2)* – in contrast to Type 1, this ore type contains cuprite, malachite and azurite as the main copper oxide minerals. Predominantly contains carbonaceous gangue, and usually, significant amounts of clay-like slimes.
- iv. *Mixed copper sulphide/oxide ores* – these contain varieties of both sulphide and oxide minerals, and are the most complex copper-bearing ores from a beneficiation point of view. The major copper minerals present in this ore type include bornite, chalcocite, covellite, azurite, malachite, cuprite, and chrysocolla. Significant amounts of cobalt minerals may also be present in this ore.
- v. *Copper oxide gold ores* – this ore type is not abundant but is of significant value because it contains gold. The few known deposits are in Brazil and Australia. Copper in these ores is represented by cuprite, native copper, antlerite and tenorite. The gold is associated with cuprite, as an auricupride and several sulphosalts. The major problem associated with treatment of this ore type is the presence of large amounts of clay slimes in the form of iron hydroxide and illite.

4.2. Flotation Properties of Individual Copper Minerals and Mixtures

According to [27] the flotation characteristics of oxide copper minerals from natural ore are dependent on a number of factors, some of which include:

- 1) Chemical composition and physical structure of the oxide copper minerals and the ionic composition of the slurry phase play important roles in the floatability of various oxide minerals. The oxide minerals are often porous and in some cases, water soluble. Some of the oxide minerals tend to slime during grinding, and flotation of fine oxide minerals is to a greater extent difficult.
- 2) The gangue constituents and their nature are sometimes determining factors in the selection of a treatment a treatment process for beneficiation of oxide copper ores. Highly weathered ores usually contain a fairly large amount of slimes, which has a negative effect on the floatability of oxide copper minerals. Also there is an appreciable difference in floatability between oxide minerals from carbonaceous and siliceous ores.
- 3) The mechanical strength of the surface layers of many of the oxide copper minerals is weak. Therefore, flotation of oxide copper ores using sulphidisation method, can improve by reducing turbulence and attrition within the flotation cell.

Malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) is one of the most important oxide copper minerals for production of copper from

oxide ores using flotation. Various flotation methods have been examined by a number of researchers [29; 30; 8; 17]. In a number of oxide ores, cuprite (Cu_2O) is present as a secondary mineral together with sulphides, malachite and tenorite. Cuprite can be floated using either sulphidisation or anionic flotation methods. The flotation properties are to a less extent different from those of malachite. For example, using a sulphidisation method for flotation of cuprite requires higher dosages of the sulphidiser. Laboratory studies conducted on these types of ore indicated that improved metallurgical results can be achieved by using the sulphidisation method with an ester-modified xanthate [31]. Tenorite (CuO) is usually present in mixed copper oxide sulphide ore. The flotation properties of tenorite are similar to those of cuprite. Azurite ($\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$) usually appears in small quantities together with malachite in a number of deposits in Zambia and the Democratic Republic of Congo. Plant and laboratory data showed that azurite has similar flotation properties as malachite [27]. Chrysocolla (CuO_xSiO_2) is the most studied of all the oxide copper minerals. Numerous researchers have carried out extensive laboratory studies [32; 33; 34]. Laboratory research work has shown that chrysocolla can be floated using the sulphidisation method, as shown in Figure 6 or by hydroxamate collectors. However, none of these processes have been applied at an industrial scale, since chrysocolla is usually concentrated using hydrometallurgy.

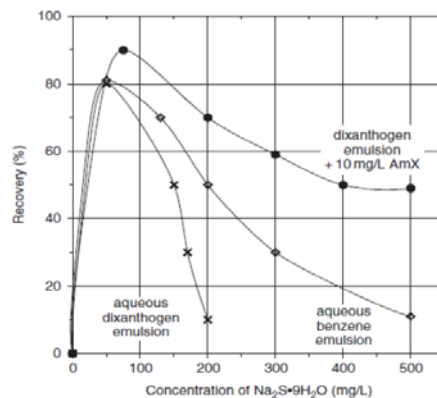


Figure 6: Effect of Na_2S on the flotation of Chrysocolla [27].

4.3. Flotation Practice in the Beneficiation of Oxide Copper Minerals

Selection of reagent scheme for the beneficiation of oxide copper ores depends on a number of factors and some of the important ones are:

- 1) Type of oxide copper minerals present in the ore.
- 2) Type of gangue minerals - some ore types contains silicate gangue free of slimes, which are the most amenable to flotation. Ores with dolomitic gangue can be beneficiated using sulphidisation only. In general, each ore type requires the selection of different reagent schemes.
- 3) Degree of liberation - the relatively fine-grained ores are more amenable to flotation than the finely disseminated ones, which require finer grinding.
- 4) Chemical composition and physical structure of the copper minerals play an essential role in the floatability of oxide copper minerals [35].

From plant practice, the treatment of oxide copper and copper cobalt ores is being carried out by the following methods: a) Sulphidisation flotation method, b) The carboxylic/ fatty acid process and c) The use of alkyl hydroxamates/ chelating reagents.

4.3.1. The sulphidisation process

This process was first applied on lead carbonate ores and is now the most widely used method in the beneficiation of oxide copper-bearing ores. The reagent schemes used to treat oxide copper ores, mixed copper sulphide oxide ores and oxide copper/cobalt ores varies from one ore type to the next, mainly by type of collector and sulphidiser used. The choice of reagent scheme depends largely on the type of natural ore to be treated. The three main reagents used in beneficiation of oxide copper and copper cobalt ores include sulphidisers, collectors and modifiers/depressants [36; 17; 27]. It is reported to be preferable to other processes like the fatty acid process as it is more selective and not limited to certain types of gangue minerals. The most preferred sulphidiser used in flotation of oxide copper minerals is $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. Other sulphidisers used in operating plants include NaHS and $(\text{NH}_4)_2\text{S}$. Previous studies have reported that higher dosages of NaHS are required to achieve activation of malachite [27]. The authors of [28] noted that the sulphidisation method using xanthate collector is sensitive to the following major factors:

- i. Rate of sulphidiser additions must be carefully controlled to obtain optimum sulphidisation and prevent excess SH^- ions that may cause depression.
- ii. Sometimes higher additions of sulphidiser are required, especially if the ore contains excessive amounts of slimes.

The consumption rate of sulphidiser also depends on the type of collector used. When using xanthate only, the sulphidiser rate is much higher than when using certain secondary collectors, such as dithiophosphates. It was noted by [27] that the selection of a sulphidiser is based on the consumption required for flotation of oxide copper from particular ore types. Figure 7 shows the effect of different sulphidisers.

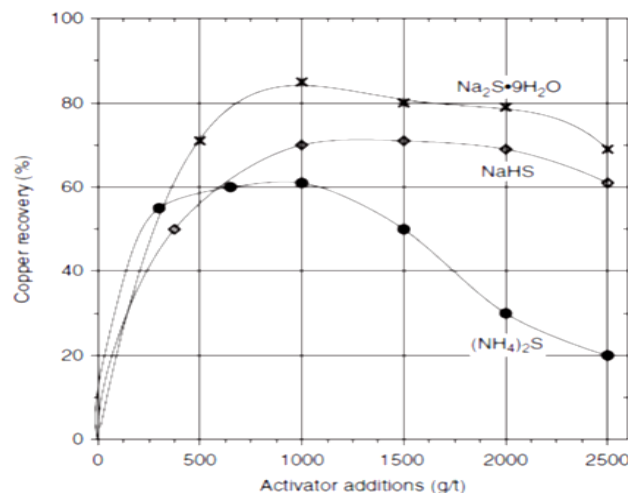


Figure 7: Effect of levels of different sulphidisers on copper flotation from the Kolwezi open pit (Congo,

Africa) [27].

Figure 7 showed that the highest copper recovery was achieved by using $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ as the sulphidiser. As such, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ is the most preferred sulphidiser used in the flotation of oxide copper minerals.

Dispersion of the gangue is normally realised by conditioning the feed with sodium silicate (Na_2SiO_3). However, in the past two decades, new depressants have been developed and introduced into a number of operating plants. Some of these depressants include: a mixture of sodium phosphate and lignin sulphonate (depressant 3XD), a mixture of low-molecular-weight acrylic acid and sodium silicate (depressant 2D) and hydrosol based on the reaction of sodium silicate with alumina sulphate (depressant SD). These depressants were extensively examined on copper oxide ores from the Nchanga mine in Zambia. Figure 8 shows the grade-recovery relationship using the different depressant combinations.

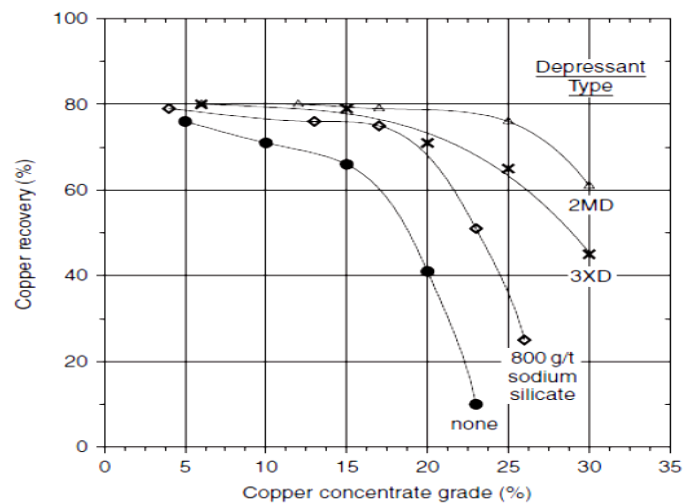


Figure 8: Effect of levels of various depressants on copper grade-recovery relationship from Nchanga open pit ore [27].

From the graphs, depressants 3XD and 2MD showed excellent dispersion of gangue.

It was reported by [37] that sulphidisation in the treatment of oxide ores was first developed with industrial success on Pb-Zn oxide ores in Australia. The method involves multistage addition of sodium sulphide (Na_2S), sodium hydrosulphide (NaHS), or ammonium sulphide ($(\text{NH}_4)_2\text{S}$), together with xanthate collectors such as potassium amyl xanthate (PAX) [15]. When induced in the slurry, the sulphidiser dissociates into the species H_2S , HS^- or S^{2-} depending on the pH. These ions react with the copper oxide minerals, to form a sulphide layer on the surface of the mineral particles.

The authors of [20] investigated on the efficiency of oxide copper-cobalt ores flotation by combination of sulphidisers. Sodium hydrosulphide and ammonium sulphide, were used as sulphidisers to enhance flotation selectivity of copper and cobalt towards the gangue minerals. The investigation showed that sodium hydrosulphide exhibited a good selectivity of copper and cobalt flotation towards gangue minerals. On the other

hand, ammonium sulphide induced higher metal recoveries with very low selectivity. However, a controlled addition of a 1/1 combination of sodium hydrosulphide and ammonium sulphide showed the best sulphidising effect in regard to the quality of produced concentrates and the related recovery of valuable metals, that is, 80% of copper and cobalt were recovered with a concentration ratio of 3.5. Potassium amyl xanthate (PAX) was used as the main collector, strengthened by a secondary collector, an emulsion of a mixture containing 90 wt% gasoil and 10% hydrolysed palm oil. Sodium carbonate was added in the proportion of 10% of the gasoil quantity in order to stabilize the emulsion.

It was shown by [39] that sulphidisation restored the floatability of three oxidised sulphide minerals: chalcopyrite, pyrrhotite and pentlandite. At optimum sulphidisation potential of -650 mV, the flotation recovery of chalcopyrite was found to be significantly greater than that of the pyrrhotite, which in turn was found to be better than that of the pentlandite.

The authors of [40] reported that sodium sulphide and butyl xanthate flotation obtained a concentrate with 19.01% TCu and a recovery of 35.02% from a Mexican copper ore. The ore was a mixed ore containing mainly copper oxide and some copper sulphide that responded well to flotation.

Phetla & Muzenda [17] carried out a study to develop a flotation procedure for an oxide copper ore from Central Africa. The study aimed at producing a copper concentrate of grade 18% TCu from a 4% TCu feed grade. The best recovery achieved with the multistage sulphidisation procedure at high temperature and extended residence time, was 48% and 50% Cu and Co respectively. The best concentrate grade achieved was 13% TCu on de-sliming.

Dianwen and his colleagues [41] in their study on the sulphidisation promotion effect of ammonium sulphate on flotation of copper oxide ore, showed that flotation recovery increased by 12.28% when ammonium sulphate was added in the presence of sodium sulphide. The highest recovery was obtained when ammonium sulphate and sodium sulphide were in the same dosages.

Wen and his colleagues [42] reported that there was an improvement in the flotation indexes of a refractory copper oxidised ore with a copper content of 1.45% TCu, from Jinping. The study used a combination of ethylenediamine phosphate and ammonium bicarbonate as the activator, sodium sulphide as sulphidising agent, isoamyl xanthate as collector and pine oil as frother. A closed-circuit flotation test yielded a copper recovery of 76% with a concentrate grade of 21.65% TCu.

Wang and his colleagues [43] reported on the flotation of a Yunnan copper oxide ore using a combination of sodium sulphide and ethylenediamine as activators with ordinary xanthate. A closed circuit flotation test yielded a flotation concentrate of grade of 16.01% TCu and recovery of 74.38%.

Wang and his colleagues [44] carried out flotation tests on a copper oxide ore in Dali, containing 0.69% TCu copper and 11.24 g/t of silver. The ore was beneficiated by the sulphidisation-xanthate flotation method. The reagents used in the study were sodium sulphide as the sulphidising agent, and butyl xanthate and ammonium dibutyl dithiophosphate as the combined collectors. Closed circuit flotation tests yielded a copper concentrate

of grade 18.34% TCu and a recovery of 70.13%.

Mao and his colleagues[45] employed the sulphidisation flotation process on a refractory copper oxidised ore from Honghe mine. The flotation tests yielded a concentrate grade of 3.93%TCu and concentrate recovery of 64.36% with sodium sulphide consumption at 200 g/t, sodium isobutyl xanthate at 150 g/t, ethylenediamine phosphate (activator) at 60 g/t and pine oil at 75 g/t. A closed circuit flotation test then yielded a copper recovery of 57.41% with a concentrate grade of 10.85% TCu.

4.3.2. The carboxylic/ fatty acid process

A number of different collectors have been evaluated for oxide copper flotation without sulphidisation. These include organic complexing agents, fatty acids, fatty amines and petroleum sulphonates [46; 24; 47].

Despite showing promise in the laboratory tests, all these collectors have had limited success when applied to a plant situation [14]. Deng & Chen [24] reported that the limitation of some of these collectors is their lack of selectivity over carbonate gangue minerals, such as dolomite, and calcite. In addition, it was noted that some of the gangue minerals even float preferentially over the copper oxide.

The carboxylic acid process has been in use in Africa for over 50 years and has been referred to as the “palm oil” process [17]. It has been reported that around 5 million tonnes of copper oxide ores are beneficiated annually by this process, producing 25% of the copper concentrates.

A copper producer in Central Africa has been reported to use a fatty acid collector, consisting of palm oil at 75% acidity (expressed as oleic acid). It is mixed with gas oil (diesel) at a ratio of 3:1 (palm oil: gas oil). Its consumption is reported to be in the order of 1200g/t for a 6% TCu feed. The other reagents used in this process are soda ash for alkalinity and sodium silicate for gangue dispersion and depression. However, the main concern with palm oil is its lack of selectivity, particularly when the ore contains carbonate gangue minerals such as calcite and dolomite. These are collected by the fatty acid even preferentially to valuable copper minerals such as malachite. Thus, the use of the fatty acid process must be strictly limited to the treatment of siliceous ore containing only traces of carbonate gangue minerals [17].

4.3.3. The use of alkyl hydroxamates/ chelating reagents

Popperle [48] first introduced the use of hydroxamic acid or their salts as collectors in ore flotation. Fuerstanau & Peterson [49] used alkyl hydroxamates for the flotation of chrysocolla and suggested that flotation was as a result of the formation of an insoluble complex between surface metal ions and hydroxamate.

Evrard & DeCuyper [50] reported the use of alkyl hydroxamate for copper-cobalt oxide ores flotation as being advantageous. Danilova and his colleagues[51] noted the benefits of using alkyl hydroxamates to recover chrysocolla without prior sulphidisation. Lenormand and his colleagues[52] discussed the mechanism of adsorption of potassium octyl hydroxamate on malachite.

Lee and his colleagues[14] provided relevant practical aspects and guidelines to facilitate the successful application of hydroxamates in operating plants. They reported that alkyl hydroxamates are excellent collectors for well defined copper minerals such as, malachite, cuprite, tenorite, azurite, atacamite, and chrysocollas with high copper content, without any prior sulphidisation or activation. In addition, they highlighted that hydroxamates have a number of advantages over most other collectors and methods such as sulphidisation flotation, developed for recovery of oxide copper. Some of these advantages are: no special controls are needed; application is straight forward; flexibility in addition point; ease of handling and simplified flowsheet.

Laboratory flotation tests with AERO®6493 Promoter (alkyl hydroxamate) conducted by plant metallurgists of a Canadian mining company (British Columbia), on an ore assaying 0.61% TCu showed a 10% increase in total copper recovery resulting from a 30% increase in ASCu recovery. Typical ASCu recovery in the absence of alkyl hydroxamate was less than 1%. After a plant trial was conducted with AERO®6493 Promoter, trial results confirmed that 20-30% of the ASCu could be recovered using 75 g/t of the collector. Best results were achieved when hydroxamate was stage added to the rougher, scavenger and first cleaner.

Fuerstanau and his colleagues[47] in a study on the applicability of chelating agents as universal collectors for copper minerals, reported that potassium octyl hydroxamate, a water-soluble reagent, exhibited unusual potential for the flotation of oxide copper minerals.

Lee and his colleagues[25] showed that using n-octyl hydroxamate (AM28 made by Ausmelt Limited) in conjunction with traditional sulphide collectors (PAX) and methyl iso-butyl carbinol (MIBC) as a frother can successfully simultaneously recover copper sulphides and oxides by flotation from blended ore minerals. The blend used in this laboratory scale investigation was 70% sulphide ore and 30% oxide ore on a weight basis. The copper sulphides present in the blend were bornite and chalcopyrite, while the oxides were malachite and minor azurite. Study showed that AM28 successfully recovered malachite and minor azurite, which were present in Minto's oxide ore without adversely affecting the sulphide recovery for the blend composite.

Parker and his colleagues[53] utilised electrochemistry, vibrational spectroscopy and x-ray photoelectron spectroscopy to investigate the interaction of KH n-octahydroxamate with sulphide minerals chalcocite, pyrite, chalcopyrite, covellite and bornite. Each of the techniques showed that a multilayer of cupric hydroxamate formed on chalcocite, bornite and chalcopyrite conditioned in the hydroxamate collector, and visual inspection revealed that the multilayer had rendered the minerals hydrophobic. Consumption of hydroxamate by non-target minerals (such as oxidised pyrite) was also observed. These minerals also reported to the concentrate and this indicated a possible application of hydroxamates in the flotation of mixed sulphide oxide ores.

Xiong and his colleagues[54] used a hydroxamate collector in conjunction, with potassium amyl xanthate (PAX) in the flotation of low-grade copper oxide ores from DongChuan mine. From the series of laboratory scale rougher flotation tests conducted, the highest copper recovery obtained was 78.9% at a concentrate grade of 2.5% TCu using AM28 dosage of 740 g/t and PAX dosage of 20 g/t. with one stage of cleaning, the copper grade increased to 9.6% TCu with the copper recovery at 64.9%.

Xiong and his colleagues[55] conducted a series of bench-scale flotation tests on refractory oxide copper ores from Yangla Mine. Potassium amyl xanthate was used as the sulphide collector and a chelating reagent, hydroxamate AM28 was used as the oxide collector. It was reported that AM28 successfully recovered all the discrete copper oxide minerals from the Yangla ore. The rougher flotation tests yielded an average copper recovery of 38.4% with a concentrate grade of 3.19% TCu.

Numprasanthai [5] investigated on chrysocolla flotation using n-octahydroxamate collector. Dry chrysocolla grinding yielded a copper recovery of over 97% and wet chrysocolla grinding yielded copper recovery of up to 99.1%.

5. Conclusion

The concentration of oxidic copper minerals is largely being done by the sulphidisation method and the use of alkyl hydroxamates/chelating reagents. It is evident from the literature that hydroxamates have a number of advantages over most other reagents and methods such as sulphidisation flotation, developed for the recovery of oxidic copper minerals. Some of these advantages are: no special controls are needed; application is straightforward; flexibility in addition point; ease of handling and simplified process flow-sheet.

6. Recommendations

A limitation of the study was the lack of flotation reagents, particularly the hydroxamates. For this reason, these findings cannot be generalised for the concentration of all oxidic copper minerals on this study alone. As such, it is recommended to carry out flotation of mixed oxide/sulphide ores from the Zambian Copperbelt with hydroxamates to determine their flotation response to this reagent and therefore.

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