

# Sustainable Use of Copper Resources: Beneficiation of Low-Grade Copper Ores

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**Abstract:** The global market has announced copper as a modern energy metal and finds its extensive utilization in the construction industry, electrical wiring, power transmission lines, alloying, anti-corrosive coating, heat exchangers, refrigeration tubing, etc. Copper ore is primarily beneficiated from sulphide mineral deposits. Due to high-grade copper sulphide deposit exhaustion, the focus has now shifted towards recovery from different lean-grade oxide and mixed ore deposits. The present paper summarizes the utilization of copper as a clean energy mineral and its importance in the current renewable energy sector. Extensive research has been carried out on the flotation of copper sulphide ore as compared to copper oxide and mixed type ores. Besides flotation, other beneficiation techniques (selective flocculation and gravity separation) are also discussed in the present review. A few novel pretreatment methods are currently being studied for copper ore to intensify the separation for higher productivity.

**Keywords:** copper ore; flotation; mixed collector; gravity separation; battery minerals

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## 1. Introduction

Red metal “copper” is currently visualized as a clean energy metal. Specific properties such as conductivity, ductility, efficiency and recyclability are primary drivers for qualifying copper as a critical material for renewable energy (solar and wind technology). It also has significant energy storage usage (flow battery, lithium-ion battery and sodium battery) in the electric vehicle production sector. Again, the electricity generation from solar and wind energy uses four to six times more copper than fossil fuel (non-renewable resources), which partially reduces the non-renewable energy consumption [1,2]. A wind turbine system of three megawatts (MW) power capacity consists of 4.7 tons of copper, while, in the case of the solar power system, 5.5 tons of copper is needed per MW production [3,4]. Again, lithium-ion battery and flow battery for one MW of energy storage requires 44 lbs. and 540 lbs. of copper, respectively [4,5]. The utilization of electric vehicles (EV) is becoming a trend, as it causes less/no environmental pollution and reduces/eliminates fuel consumption costs and energy independence, whose function depends heavily on copper (Figure 1) [1,3,5]. Thus, the increasing demand for EVs will ultimately affect copper production. By 2027, the copper requirement is supposed to be expanded by 1700 kt [5]. According to the world bank report, copper has become an imperative element due to its wide application in evolving low-carbon technology (Figure 2) and in technology-based mitigation scenarios, which will ultimately generate a low-carbon future [3]. However, the International Copper Association (ICA) also listed advantage copper applica-

tions in renewable energy, climate change mitigation and adaptation and many sustainable developments, which is impossible for any other metal or material [4,5]. Its recyclability without losing its inherent property after recycling provides a better economy and strong life cycle analysis, which is impossible for other materials consumed and that become noneconomic at the end of life [4]. The importance of copper can also be visualized from ancient history, where it lasted the whole 1000-year era named the “Chalcolithic Period” or “Copper age”, from 4500 BC to 3500 BC. It has been reported that more than 80% of the total production of copper mined throughout history is still in use [6]. Thus, copper is a critical modern mineral for new generation technology advances [7,8].

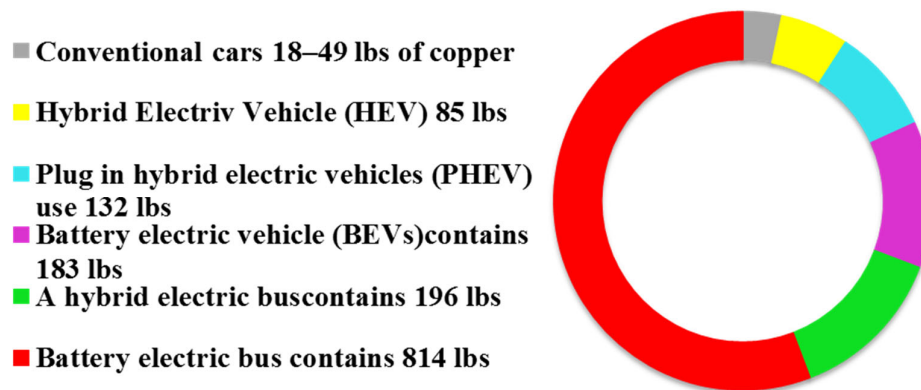


Figure 1. Copper use by different types of vehicles (adapted) [4].

	Wind	Solar	Photovoltaic	Concentrated solar power	Hydro	Geothermal	Energy Storage	Nuclear	Coal	Gas	Carbon capture and storage
Aluminium											
Chromium											
Cobalt											
<b>Copper</b>											
Graphite											
Indium											
Iron											
Lead											
Lithium											
Manganese											
Molybdenum											
Neodymium											
Nickel											
Silver											
Titanium											
Vanadium											
Zinc											
<b>Total</b>	<b>10</b>	<b>8</b>	<b>2</b>	<b>8</b>	<b>6</b>	<b>11</b>	<b>11</b>	<b>9</b>	<b>8</b>	<b>6</b>	

Figure 2. Mapping of minerals with their relevance in low-carbon technology [3].

The complete dematerialization of rich-grade copper ore and the continuously increasing demand make the processing of lean-grade resources inevitable and mandatory to sustain industrial growth and development. According to the global statistics, copper

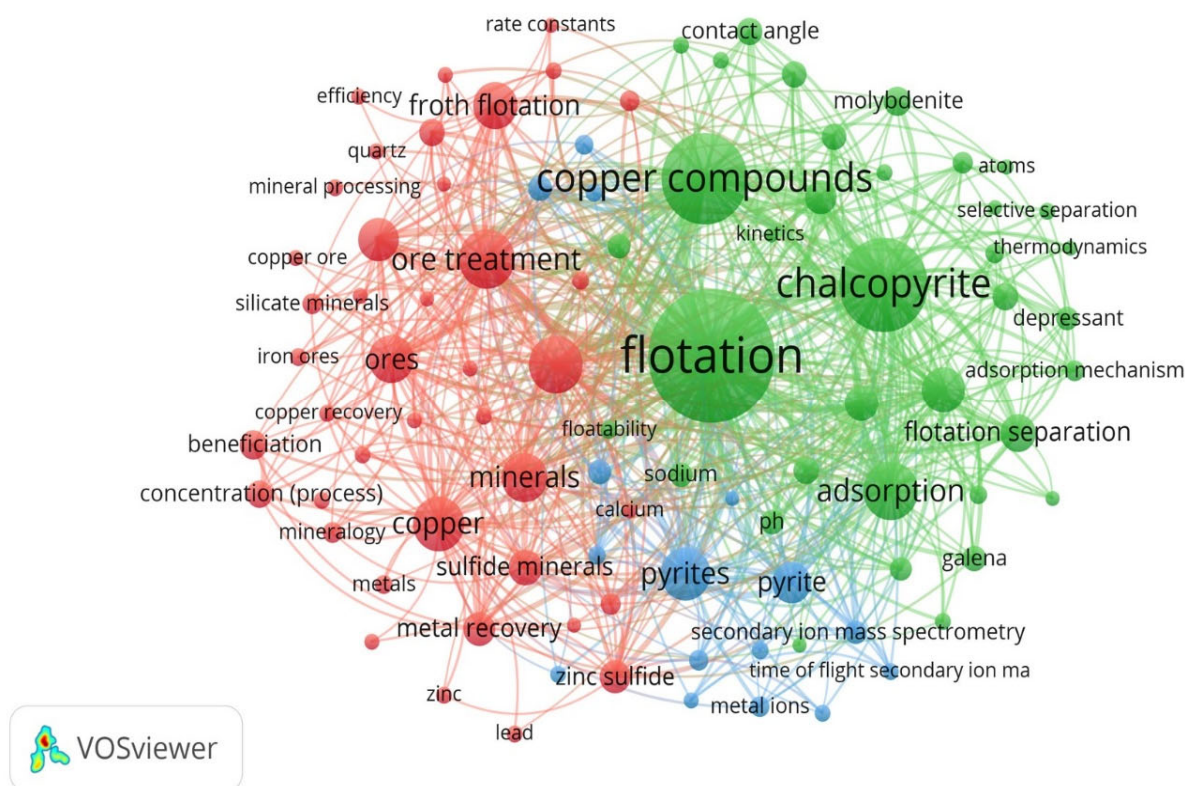
is in the third position among all metals in global consumption, behind steel and aluminum. Most of the copper deposits worldwide are porphyry in nature and contribute 50–60% of the total global copper production. These deposits consist of primarily copper sulphide minerals such as chalcopyrite ( $\text{CuFeS}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ) and enargite ( $\text{Cu}_3\text{As}_5\text{S}_4$ ). Estimates suggest that approx. 90% of copper is derived from sulphide deposits, mostly chalcopyrite, accounting for about half of all copper production [9]. In a few deposits, copper also occurs in the form of oxide (cuprite- $\text{Cu}_2\text{O}$ ), malachite- $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ , azurite- $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ , chrysocolla- $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$  and a mixed form, i.e., both copper oxide and sulphide minerals [10,11].

Copper is a non-ferrous base metal, which comprises 50 ppm on average in the Earth's crust [12]. The average grade of a copper deposit for exploitation is approx. 0.4% (open cast mines) and 1–2% Cu (underground mines), with many other valuable minerals and gangue minerals [12]. Flotation is the most extensively used conventional technique for copper beneficiation [13–15], particularly sulphide minerals [16,17]. Flotation has been carried out using different reagents, which involves differences in the physical and chemical surface properties of copper minerals and gangue to separate them from each other by using various surfactants [18–20]. Besides flotation, gravity separation [21–24], leaching [25] and selective flocculation [26–28] have also been used for the processing of copper ore.

It is evident in the literature that there is a lack of information on copper flotation, and most of the literature is confined to sulphide ore. The processing of oxide and mixed ores is minimal. The aim of this paper is to review the published papers on the flotation of copper ore with reference to different mineralogy and recently developed pretreatment methods to intensify the separation. Different beneficiation techniques for copper ore are discussed, and prospects for further research are identified. It should be noted that topics such as recovery aspects of copper from secondary resources or hydrometallurgical and pyrometallurgical processes in copper extraction are not included in this review.

## 2. Visualization of Recent Research Trends of Copper Using Bibliographic Analysis

Sections 4.1–8.3 will explain the detailed work on copper ore beneficiation within different categories. Visualization and evaluation help in reviewing and assessing the essential findings and explaining reciprocity/interactions, trends and models. The current section focuses on the present scenario of the copper ore literature, which can lead to future research. The bibliographic analysis involves the authors' research interest, the total number of papers published by the researchers and their total citations. The VOS Viewer tool [1] was used to establish and visualize the bibliometric network of scientific literature on copper ore processing. For a bibliographic analysis, the data was generated using the SCOPUS search engine for the articles published in journals during the 10 years (2010–2020) (excluded articles were published in conference proceedings, seminars or reports). The publication data files are arranged into three categories (i.e., keyword, article author and publishing country), contained around 427 publications. An analysis of these data files via VOS viewer created a map of text patterns (Figure 3) to recognize the dominating research trends, especially as per the significance and frequency of the keyword search during a literature survey. From the mapping, it is confirmed that flotation is the most current trending and vigorously practicing research areas in copper ore beneficiation.



**Figure 3.** Text pattern analysis during the last decade (2010–2020) literature survey to visualize its scientific trends (more occurrences in larger circles).

### 3. Global Copper Reserve, Demand and Production and Consumption

According to the USGS (United State Geological Survey) report in 2018, Chile has the highest copper reserve, followed by Australia, Peru, Russia, Mexico and the United States [29]. Apart from the above major countries, Indonesia, China, Kazakhstan, DR Congo and Zambia also contribute significantly towards the world copper reserves [29,30]. The total copper reserve is estimated to be about 720 Mt. Again, the non-estimated and identified resources are calculated to be around 3500 Mt and 2100 Mt, respectively, excluding the copper resources present in the deep marine environment. Figures 4 and 5 show the pictorial representation of the world copper reserve, mine production [31] and global copper reserves by different countries [29].

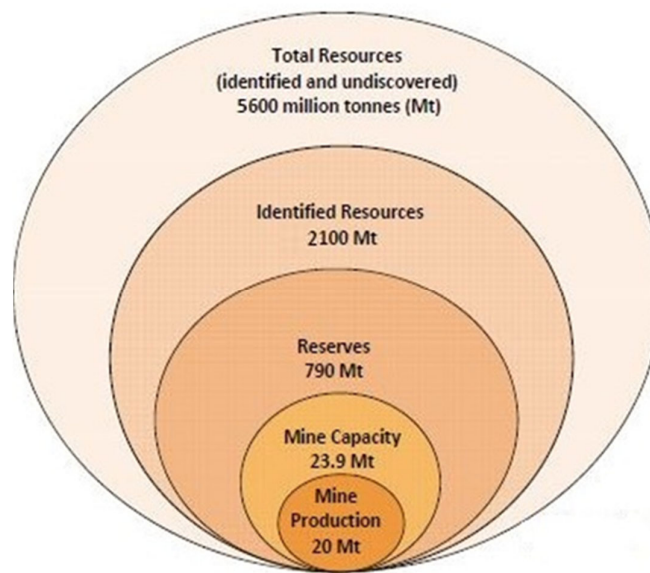


Figure 4. World copper reserve and mine production [31].

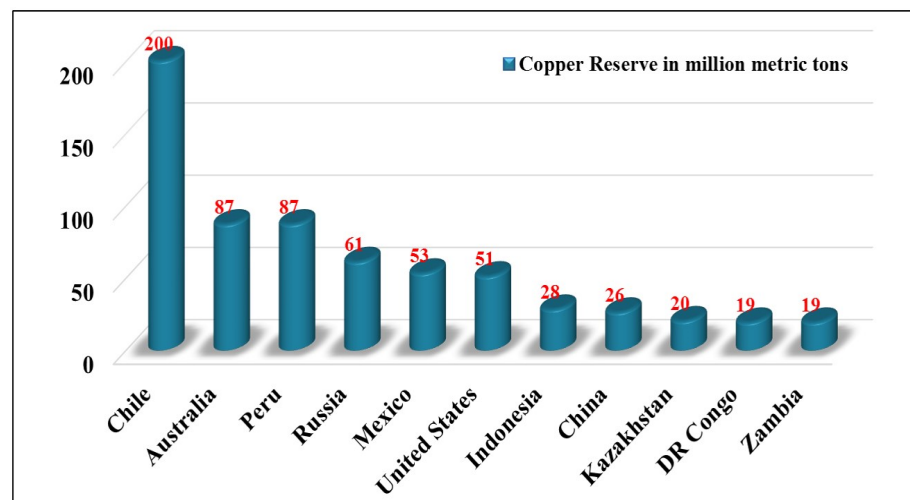


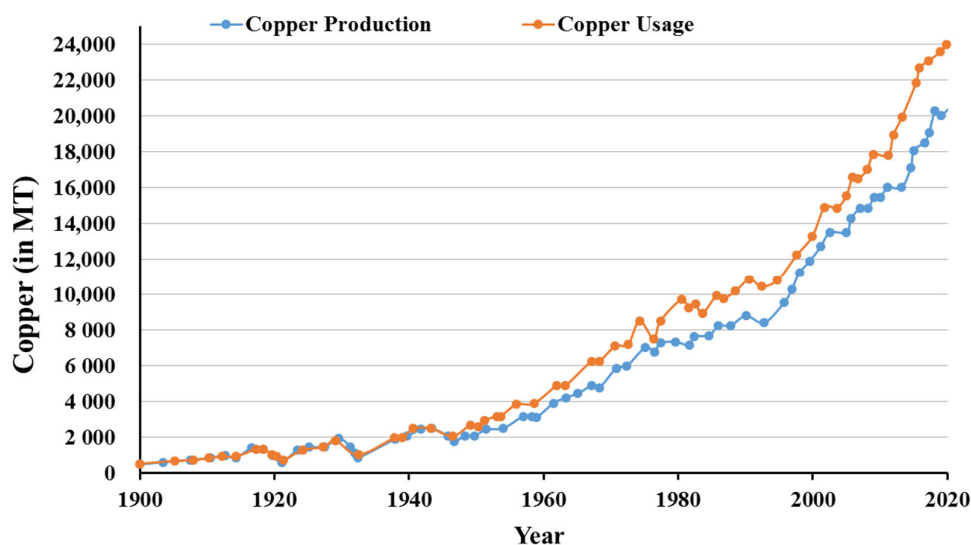
Figure 5. Global Copper Reserves as of 2019 by country [29].

The worldwide copper mine production decreased marginally from 20.4 Mt in 2018 to 20 Mt in 2019. The major factor attributed to this slight decrease in production is relocating the Grasberg and Batu Hijau mines in Indonesia to a new ore zone [32]. Due to the off-grade ore, unsuitable climatic conditions and workers strike, there is a decrease in Chile's copper production. However, the overall refined copper production increased marginally to 25 Mt in 2019 from 24.2 Mt in 2014. In China, the production of refined copper has declined because of the shutdown of many smelters for maintenance and development purposes. Zambia's refined production was heavily affected by a new construction assignment on copper concentrate, which ultimately reduced the smelter output. An insignificant supply of sulphuric acid fails to generate the desired electrowon copper. The mine production of various countries is tabulated in Table 1 [32].

**Table 1.** The world mine production by various countries [32].

Country Name	Mine Production (kt)	
	2018	2019
United States	1220	1300
Australia	920	960
Chile	5830	5600
China	1590	1600
Congo [Kinshasa]	1230	1300
Indonesia	651	340
Kazakhstan	603	700
Mexico	751	770
Peru	2440	2400
Russia	751	750
Zambia	854	790
Other Countries	3540	3800
World Total (Rounded)	20,400	20,000

According to an ICSG report in 2019, the global total copper consumption increased to 24,500 MT in 2018 from 17,888 MT in 2008 and 5000 MT in 1900, indicating a compound annual growth rate of 3.4% a year for usage over these periods (Figure 6) [29,31]. Most of the refined copper is consumed by China (49%), followed by other Asian countries (20%), Europe (18%) and America (12%) [29]. As per the Fitch forecast, the world copper demand will increase by 2.6% by 2027.

**Figure 6.** World copper production and usage for 1900–2020 [31].

#### 4. Copper Mineralogy

Considerable knowledge and understanding of copper mineralogy is imperative because of its varying geological occurrences. In the Earth's crust, copper occurs in combinations with iron, sulphur, carbon and oxygen. Its occurrence is classified into three groups as primary hypogene deposits, secondary group deposits and tertiary group deposits [33].



Porphyry deposits are more common deposits for copper ore formed by the hydrothermal fluids emanating from a magmatic chamber located several kilometers deep. The mineralization of a hydrothermal deposit is structurally controlled with stock work of quartz veins, vein sets, fractures and breccias containing copper sulphide with gold or molybdenum [9]. The associated valuable minerals are pyrite, arsenopyrite, galena, sphalerite, molybdenite, cobalt, pyrrhotite, hematite, magnetite, silver, gold, PGE minerals, uranium and antimony in different deposits, based on the origin. Silicates are the primary gangue minerals (quartz, feldspar, albite, mica, etc.) in most copper deposits. Processing such multimetal ores to produce individual mineral(s) of the desired quality is extremely tough. The challenges during beneficiation become manifold if it contains a higher amount of impurities. The world's copper deposits (Figure 7), along with the associated minerals, are listed in Table 2. In addition, the major copper minerals are listed in Table 3.

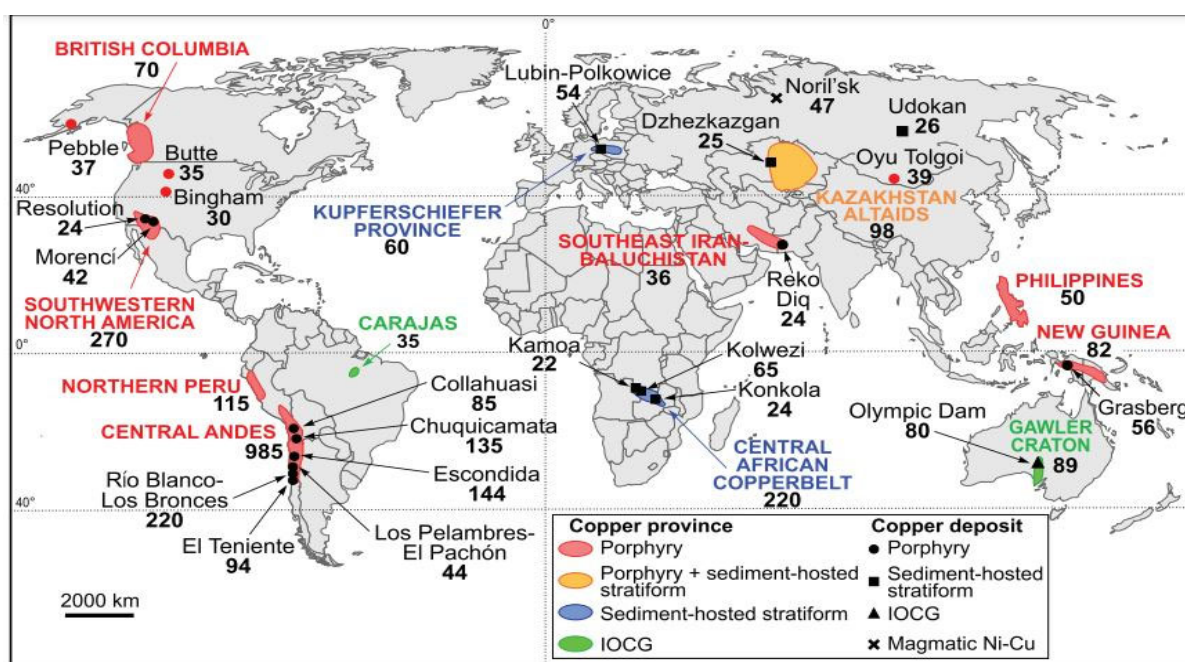


Figure 7. World map depicting important copper deposit [34].

Table 2. Types of major copper deposits [11,33,35,36].

Deposit Type	Description	Major Minerals	Examples
Porphyry	Large, low-grade stock work disseminated deposits	Primary-Chalcopyrite, bornite. Secondary-Chalcocite, covellite, malachite, azurite, cuprite, molybdenum. By-product material: Rhenium, gold, silver, and tin.	Chuquicamata and La Escondida, Chile; Bingham Canyon, USA; Grasberg, Indonesia; Malankhand deposit; India
Sediment-hosted	Strata bound disseminations of copper minerals occurring in a range of sedimentary rock.	Chalcocite, bornite with lesser chalcopyrite, galena, pyrite and hematite. By product material: zinc, silver, cobalt	Nchanga, Zambia; Lubin, Poland; White Pine, USA; Khetri deposit, India
Red-bed	Copper mineralization occurring in oxidized zones in sedimentary and volcanic rocks	Copper sulphide (1–4% Cu) with silver and rhenium.	Dzhezkazgan, Kazakhstan; Mantos Blancos, Chile
Volcanic Massive Sulphide [VMS]	Mineralization hosted by submarine volcano-sedimentary sequences	Chalcopyrite, sphalerite, pyrite, lead, gold, silver. Cobalt, tin, manganese, cadmium, bismuth	Bathurst and Kidd Creek, Canada; Rio Tinto, Spain

Magmatic Sulphide	Sulphide concentrations associated with a variety of mafic and ultramafic magmatic rocks	Primarily Chalcopyrite with Pyrrhotite, Pentlandite. Minor amount of PGE, galena, sphalerite, gold, silver, magnetite.	Sudbury and Voisey's Bay, Canada; Noril'sk-Talanakh, Russia; Kambalda, Australia
Deposit type	Description	Major mineral found	Examples
Epithermal	Vein stock works and breccias associated with high-level or near surface volcanic-related low temperature hydrothermal systems	Chalcocite, covellite, bornite, native gold, chalcopyrite	El Indio, Chile; Lepanto, Philippines; Monywa, Burma
Copper Skarns	Mineralization by chemical alteration associated with intrusions into carbonate rocks	Copper (Chalcopyrite, bornite and tennantite)	Ok Tedi, Papua New Guinea; Copper Canyon, USA; Rosita, Nicaragua
Vein Style	Mineralized structures often developed along fractures varying from centimeters up to tens of meters wide from a variety of sources	Chalcopyrite, bornite, pyrite, quartz, silver, gold, occasionally uranium, antimony and phosphorous.	El Indio, Chile; Copper Hills, Australia; Butte, USA; Singhbhum, India
Supergene	In-situ natural secondary enrichment of primary mineralization	Chalcocite, covellite, bornite	Erdenet, Mongolia; La Escondida, Chile; Sarcheshmeh, Iran
Sedimentary Exhalative	Bodies of polymetallic sulphides deposited from hydrothermal fluids vented into sedimentary basins with no obvious volcanic source	Chalcopyrite, pyrite, sphalerite, galena, pyrite, pyrrhotite, barite, silver	Broken Hill and McArthur River, Australia; Red Dog, Alaska

**Table 3.** Major copper-bearing minerals, along with their physical properties [33–40].

Mineral Name	Chemical Formula	Cu%	Specific Gravity	Hardness	Property
Native Copper (Cu)	Cu	100	8.9		Non-magnetic
Sulphides					
Chalcopyrite (Cpy)	CuFeS <sub>2</sub>	34.6	4.1–4.3	3.5–4	Non-magnetic
Chalcocite (Cc)	Cu <sub>2</sub> S	79.9	5.5–5.8	2.5–3	
Digenite (Dg)	Cu <sub>9</sub> S <sub>5</sub>	78.1	5.5–5.7		
Covellite (Cv)	CuS	66.4	4.6–4.8	1.5–2	
Enargite (Eng)	Cu <sub>3</sub> AsS <sub>4</sub>	49.0	4.4	3	
Bornite (Bn)	Cu <sub>5</sub> FeS <sub>4</sub>	63.3	4.9–5.3		Magnetic after heating
Oxides					
Cuprite (Cpr)	Cu <sub>2</sub> O	88.8	6.1	3.5–4	Non-magnetic
Tenorite (Tnr)	CuO	79.7	6.5		
Malachite (Mal)	CuCO <sub>3</sub> . Cu(OH) <sub>2</sub>	57.3	3.9		
Azurite (Azu)	2CuCO <sub>3</sub> .Cu(OH) <sub>2</sub>	55.1	3.7		
Silicate					
Chrysocolla (Ccl)	CuSiO <sub>3</sub> .2H <sub>2</sub> O	37.9	2.2	2–4	Non-magnetic

## 5. Processing of Copper Ore

According to Jonathan ward, “Without copper, we would all be living in the stone age” [12]. In the current modern 21st century, we should be thankful to copper as an essential part of many items that we use every day, such as cell phones, cars and air conditioning. From new modernized luxury to renewable energy and many countries’ integrity in their national security systems, copper is an essential commodity. The demand for copper is even predicted to rise globally in the near future. To meet the worldwide demand, its production must proceed towards sustainable growth. Previously, copper processing was quite easier because of the availability of rich-grade sulphide deposits. However, due to their continuous excavation and exploration, we are now left with off-grade sulphide deposits and many oxides or mixed deposits where the processing is complicated. This section included different ways of copper processing and its beneficiation.



For copper beneficiation, flotation is the most conventional method that has been used since 1905. Flotation, in fact, has allowed mining of the lean and complex ore bodies that would have otherwise been discarded as noneconomic overburdens [37]. The flotation enrichment technique for copper minerals was first applied to recover sulphide minerals such as galena, sphalerite, chalcocite, chalcopyrite and pyrite [38].

### 5.1. Gravity Concentration or Separation

Despite achievement by flotation, gravimetric separation techniques are still performed because of their low cost of installation and higher efficiency. However, it can be used only if there is a marginal difference between the specific gravity of the desired value mineral and the gangue. Gecamines have performed upgrading of copper–cobalt ores from Anaconda mines in Montana (USA) using gravity separation. The gravity concentration circuit contained Hancock jigs and a shaking table. After beneficiation, the copper grade increased from 8.5–9.5% to 24–27%, respectively. The recovery was also increased from 50 to 54%, respectively [41].

It should be mentioned that, for coarser size fractions, gravity separation using a table and spiral is more suitable. However, for finer-sized fractions, the application of enhanced gravity separation is more appropriate [40,41]. In numerous plants in Katanga, a gravity concentration unit is used to recover copper by reprocessing previously stockpiled copper–cobalt tailings [42,43]. Again, the concentration criterion is an essential metric for deciding whether the gravity concentration is feasible or not. Another research paper studied the gravity separation process's feasibility as a preconcentration step for lean-grade mixed copper of the Malanjkhand area using a Mozley Mineral Separator on the laboratory scale [39]. The Malanjkhand deposit contained 0.48% Cu, and the copper content was attributed mainly to chalcopyrite followed by bornite, digenite, covellite and malachite. Further, the sample analyzed 74.12% SiO<sub>2</sub> with quartz as the primary gangue mineral. The concentration criterion for valuable minerals at the Malanjkhand deposit against gangue (i.e., quartz) has been calculated and is shown in Table 4. In this case, gravity separation is feasible, as the concentration criteria are between 1.75 and 2.73. The copper grade has been increased from 0.48 to 5.33%, with 26.14% recovery [39]. To justify this result, the authors have performed preconcentration via gravity separation using a bench-scale Wilfley table for the Malanjkhand copper sample. They found that it is possible to generate a high-quality feed for flotation with 52% silica rejection and 53.68% separation efficiency. A concentrate with 2.79% Cu was produced with 66.24% recovery [40]. In a few case studies, gravity separation is rigorously used in processing copper tailings, which is discussed in Section 6. The gravity concentration of copper ores is not effective due to the poor liberation and finer grain size. The gravity concentration is feasible and effective at a coarser particle size with a higher value of concentration criterion rather than a finer particle size with the minimum concentration criterion. However, there is a scope for recovering copper-bearing minerals from low-grade deposits by using enhanced gravity separation, which needs further research.

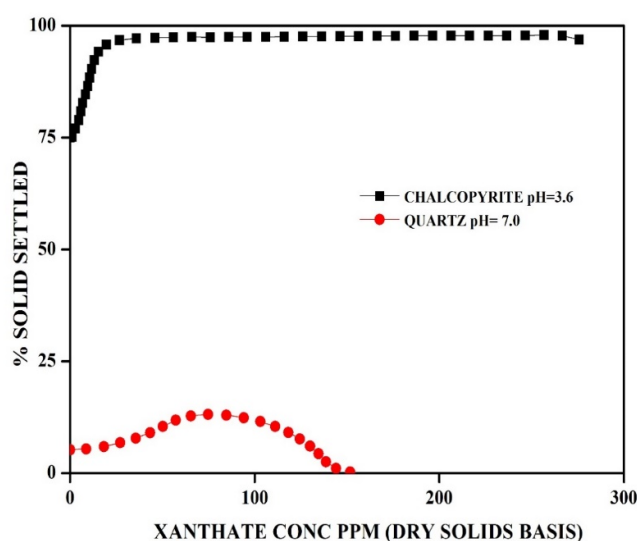
**Table 4.** Concentration criteria between Malanjkhand constituent minerals.

Specific Gravity		Concentration Criterion (CC)
Valuable Heavy Minerals	Gangue/Lighter Mineral	
Chalcopyrite = 4.1	(Primarily Quartz) Quartz = 2.65	1.87
Malachite = 3.9		1.76
Covellite = 4.6		2.18
Chalcocite = 5.5		2.73
Bornite = 4.9		2.36
Digenite = 5.5		2.73
CC > 2.5, Gravity separation is easy; CC < 1.25, Gravity separation is not feasible		

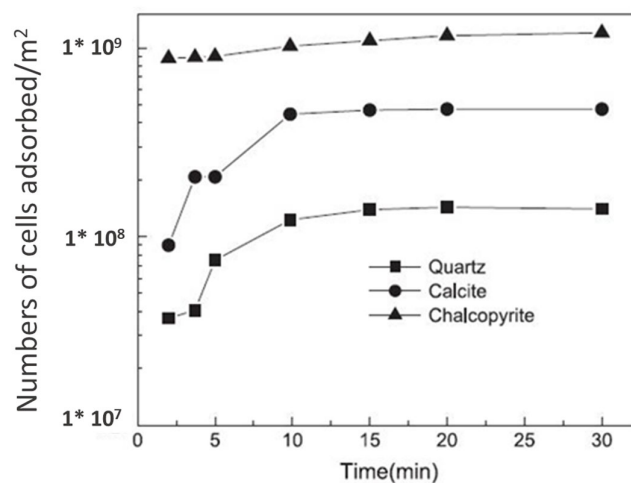
$Q_{\text{fluid}}$  (specific gravity of water = 1); Valuable/Heavy Minerals— $Q_{\text{HM}}$ ; Gangue/Lighter Mineral— $Q_{\text{LM}}$ ;  
 $CC = \frac{\rho_{\text{HM}} - \rho_{\text{fluid}}}{\rho_{\text{LM}} - \rho_{\text{fluid}}}$

### 5.2. Selective Flocculation

In some cases, conventional flotation is inefficient to upgrade the finely disseminated copper ores [44]. In such cases, selective flocculation may become a convenient technique for separating the valuable minerals from undesired gangues [45]. Sresty and Somasundaran investigated chalcopyrite–quartz’s flocculation using hydroxypropyl cellulose xanthate, and they confirmed the effective flocculation of chalcopyrite (Figure 8) without affecting quartz [45]. Patra and Natarajan [26] studied the separation of chalcopyrite from quartz and calcite using a bio-flocculant (*Bacillus polymyxa*). The adsorption studies affirmed that a chalcopyrite surface has the highest adsorption density of bacterial cells, and hence, it is selectively flocculated by leaving the quartz in a dispersed state (Figure 9) [27]. Attia and Kitchener investigated copper ore flocculation tests and concluded that the selective flocculation of copper minerals is possible by using polyacrylamide gly-oxal bis hydroxylanil [46].



**Figure 8.** Percentage of chalcopyrite and quartz settled as a function of the concentration of hydroxypropyl cellulose xanthate [47].



**Figure 9.** Adsorption density of *Bacillus polymyxa* cells in quartz, calcite and chalcopyrite as a function of time [27].

Mweene and Subramanian studied the flocculation behavior of copper ore from the Mpanda Mineral Field in Tanzania using Xantha gum (XG) as a flocculant and sodium trisilicate as a dispersant (STS) [25]. The adsorption study revealed that XG adsorbs successfully on the chalcopyrite particles, while no adsorption was reported on the silica surface (confirming the selective flocculation of chalcopyrite by XG). Finally, the Cu grade was increased from 0.9 to 19.8% by using 30 ppm of both STS and XG. Further, the separation efficiency comparison can be referred to in the literature [26]. Acar and Somasundaran studied the selective flocculation of fine chalcopyrite from pentlandite, using both polyacrylamide (PAM) and polyethylene oxide (PEO) as flocculants [28]. They reported that both minerals can be flocculated using PAM, while only chalcopyrite particles were selectively flocculated using PEO. There have been a few studies in the literature that reported on the selective flocculation of chalcopyrite and mostly confined to synthetic mixtures. However, the selective flocculation process with low-grade ore (mixture of copper minerals) behaves differently from the synthetic mixture. The selective flocculation process for recovering copper-bearing minerals from a low-grade deposit or tailing stream is still a research subject. There is a lack of understanding on the selectivity and adsorption of flocculants in copper-bearing minerals.

## 6. Flotation of Copper Ore

Since the last century, froth flotation has been applied to copper minerals, and various new developments have brought the technology to its present level. In this section, historical approaches that were practiced in copper flotation for sulphide, oxide and mixed copper minerals are discussed.

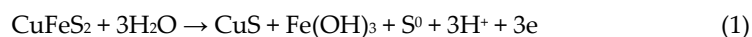
### 6.1. Copper Sulphide Minerals

The important sulphide minerals of copper include chalcopyrite, chalcocite, bornite and covellite. Among them, chalcocite (79.8% Cu) and chalcopyrite (34.5% Cu) can be categorized as the most economically important minerals [31,32,37]. It is estimated that about 90% of copper is derived from sulphide deposits; mostly, chalcopyrite accounts for approximately half of all copper production [9].

The flotation of copper sulphide ores is mainly carried out by using thiol collectors (e.g., xanthate, dithiocarbamates and dithiophosphates), which form different surface products in different copper sulphide minerals. An evaluation of the collector effects on copper sulphide was performed using the criteria of recovery and flotation rate. The flotation of sulphide minerals of copper with sulphhydryl collectors was found to be effective in the following order [46,48]: Xanthate > Dithiophosphate = Thiocarbamates > Dixanthogen.

#### 6.1.1. Chalcopyrite

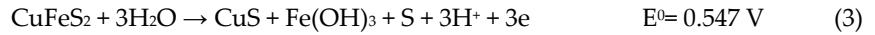
Chalcopyrite has a natural tendency to float [49–51]. Therefore, it can be floated by using a frother only in an oxidizing environment. According to Mitchell et al. [52], pure chalcopyrites exhibit an iso electric point (iep) value between pH of 5 and 6. The formation of elemental sulphur during oxidation was mainly responsible for the surface hydrophobicity and enhanced the flotation [53,54]. Thus, Gardner and Woods [53] proposed the following chemical reaction during the oxidation process at higher pH values:



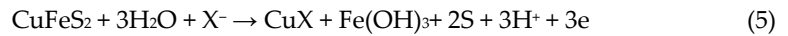
The reaction between chalcopyrite and xanthate was studied by Allison et al. in 1972 [55]. They reported that two products might be formed, i.e., metal xanthate (MX) and dixanthogen ( $\text{X}_2$ ). However, dixanthogen formation could not be detected due to the lesser insolubility of cuprous xanthate ( $\text{CuX}$ ), according to the following reaction:



According to Leppinen et al. [56], CuX can coexist with X<sub>2</sub> during the chalcopyrite and xanthate interaction. However, they stated that the presence of dixanthogen attributed to better flotation. They also concluded that the formation of CuX might take place via CuS, which was formed by oxidation:

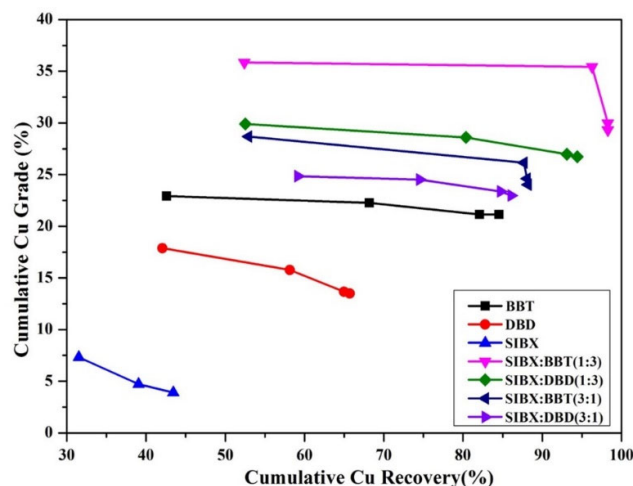


The overall reaction by combining Equations (3) and (4) is as follows:



Venugopal et al., studied the flotation characteristics of chalcopyrite ore using xanthate as a collector and pine oil as a frother [57]. They performed rougher flotation tests for the bulk feed and individual size fractions (coarser and finer). Their conclusion was in agreement with what Ram et al., reported earlier [58]. They also observed that the flotation performance was the maximum in the case of bulk flotation compared to that achieved for individual size ranges, which may be attributed to a wider size distribution in bulk feed [57,58].

Recently, Dhar et al. investigated the flotation of Nussir copper ore using three collectors: sodium Iso-butyl xanthate (SIBX), di-secondary butyl dithiophosphate (DBD), n-butoxy carbinol-o-n-butyl thiocarbamate (BBT) and their mixtures [59–61]. Nussir deposit is enriched with chalcocite and bornite as copper sulphide minerals with a liberation size of 105 µm (80% of mass). From the flotation results (Figure 10), it is observed that Nussir copper ore can float better in the sequence of BBT > DBD > SIBX. It was explained as due to the highest negative zeta potential (ZP) value observed in BBT for copper sulphides, confirming the adsorption of a negative anionic collector in metal sites that showed that BBT is the most suitable collector for Nussir copper ore. The mixed collector (BBT:SIBX::3:1) imparts a more negative ZP value compared to the individual collectors, resulting in the production of concentrates with the highest grade and recovery compared to the other mixtures [59–61].



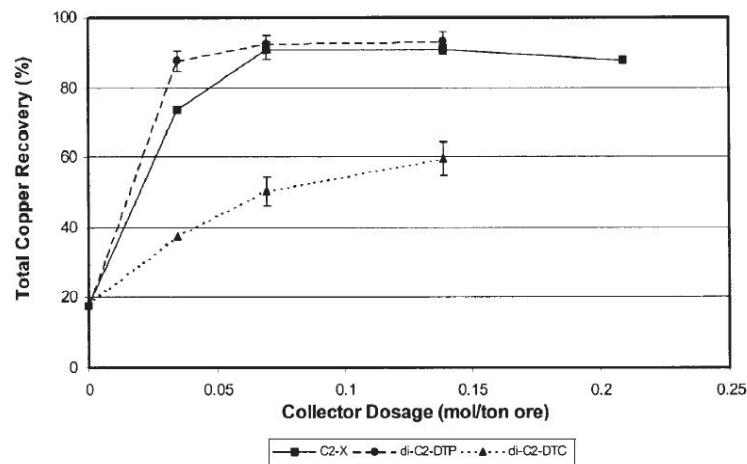
**Figure 10.** Copper recovery and grade for the three collectors (BBT, DBD and SIBX) and their mixtures in different proportion [59].

The effect of pulp aeration on chalcopyrite flotation in chalcopyrite–pyrite pulps of different pyrite contents (i.e., 20 wt%, 50 wt% and 80 wt% pyrite) with sodium iso-propyl

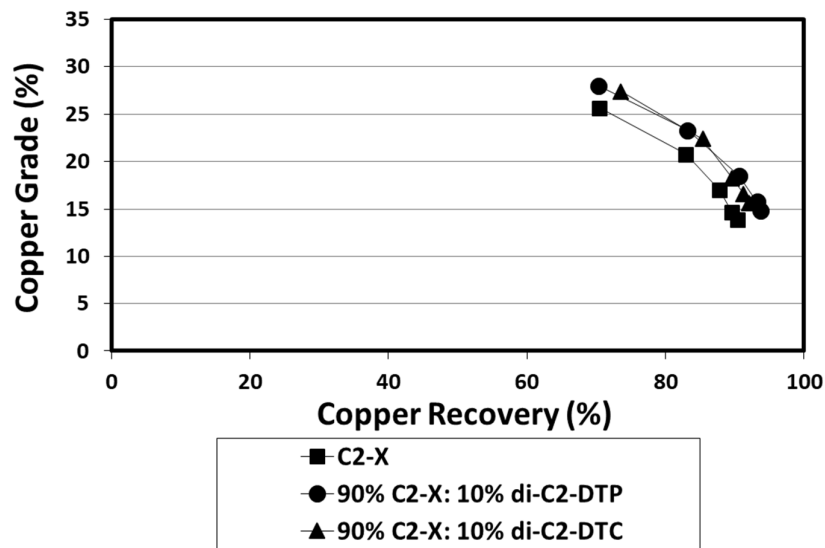
xanthate (SIPX) was investigated by Owusu et al. [62]. A significant increase in the chalcopyrite grade was observed in moderate aeration conditions, while the opposite effect was noted at a high aeration rate. There is a positive correlation between the amount of oxygen/air required for adequate chalcopyrite flotation and pyrite's weight percent in the pulp. When the weight percentage of pyrite was more than the pulp, a longer aeration time was required to facilitate xanthate adsorption on the chalcopyrite surface and its oxidation to form dixanthogen. The result concluded that chalcopyrite flotation was controlled by the ratio of hydrophobic xanthate and hydrophilic metal oxide/hydroxide produced at the solution-mineral interface [62]. Most of the studies reported earlier involved chalcopyrite mineral-dominated ores. Additionally, these studies mostly focused on the recovery aspects at different reagent suits. However, the surface oxidation of chalcopyrite may alter the adsorption phenomena and indirectly influence the floatability and kinetics. These days, there is a lot of interest in the coarse particle flotation process with different machine designs (e.g., Reflux flotation cell, Jameson cell, Hydro float separator, etc.). Therefore, detailed studies can be carried out on the floatability and kinetics of chalcopyrite with these new cells (e.g., to enhance the bubble-particle interactions in fluidized beds), as well as alterations of the hydrodynamics inside the cell to obtain a better flotation of coarser particles.

#### 6.1.2. Bornite

Hangone et al., studied the individual and combined effects of thiol collectors (xanthate, dithiocarbamates and dithiophosphates) on bornite-rich copper sulphide ore from the Okiep Copper Mine [63]. The experimental analysis found that, in the case of di-ethyl dithiophosphate (di C<sub>2</sub>-DTP; Table 5), a higher recovery was obtained (Figure 11). This was attributed to the differences in chemical reactions at the mineral surface (specifically, the lacuna/inability to form cupric-dithiolate while using di-ethyl-dithiocarbamate), which has made it an inefficient collector for copper sulphide minerals, confirming the findings of Finkelstein and Poling [64]. Higher copper recoveries were obtained using a mixed collector system, i.e., Ethyl Xanthate:Diethyl Dithiophosphate and Ethyl Xanthate:Diethyl Dithiocarbamate in a 90:10 ratio as compared to the recovery achieved with only ethyl xanthate. A relatively minor enhancement in the copper recovery and grade was observed with a mixture of Ethyl-Xanthate:Diethyl Dithiocarbamate collector in a 90:10 ratio, respectively (Figure 12). This may be due to the enhanced flotation of slow-floating particles and modified froth structure of the mixed collectors' synergistic effect [63].



**Figure 11.** The total copper recovery versus collector dosage obtained with C2-X, di-C2-DTP and di-C2-DTC in the flotation of the Okiep copper ore [63].



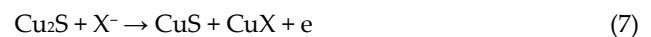
**Figure 12.** Cumulative copper grade recovery with respect to C2-X (individual xanthate), C2-X (90%):di-C2-DTP (10%) and C2-X (90%):di-C2-DTC (10%) [63].

**Table 5.** Species responsible for the surface hydrophobicity of copper minerals [63].

Mineral	Collector	Species Responsible for Hydrophobicity
Bornite (Cu <sub>5</sub> FeS <sub>4</sub> )	C2-X	CuX
Chalcopyrite (CuFeS <sub>2</sub> )		X <sub>2</sub>
Chalcocite (Cu <sub>2</sub> S)		CuX, Cu(X) <sub>2</sub>
Covellite (CuS)		X <sub>2</sub> , CuX
Bornite (Cu <sub>5</sub> FeS <sub>4</sub> )	di-C2-DTP	Cu(DTP) <sub>2</sub>
Chalcopyrite (CuFeS <sub>2</sub> )		Cu(DTP) <sub>2</sub>
Chalcocite (Cu <sub>2</sub> S)		Cu(DTP) <sub>2</sub> , Cu(DTP)
Covellite (CuS)		Cu(DTP) <sub>2</sub>
Bornite (Cu <sub>5</sub> FeS <sub>4</sub> )	di-C2-DTC	Cu(DTC) <sub>2</sub>
Chalcopyrite (CuFeS <sub>2</sub> )		Cu(DTC), Cu(DTC) <sub>2</sub>
Chalcocite (Cu <sub>2</sub> S)		Cu(DTP)
Covellite (CuS)		Cu(DTC) <sub>2</sub>

### 6.1.3. Chalcocite

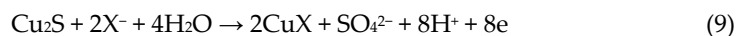
In 1979, Heyes and Trahar investigated the flotation of chalcocite using xanthate as a collector [65]. Their work revealed that the oxidation product cuprous xanthate (CuX) was solely ascribed to flotation, as the existence of dixanthogen was thermodynamically calamitous, which agreed with the findings of Gaudin and Schuman [66]. The following oxidation chemical reaction between chalcocite and xanthate was advised by Harries and Finkelstein [67]:



Further, the CuX formation mechanism was also proposed and described as the following [67]:



and





An in-depth study on porphyry copper ore using N-allyl-O-alkyl thiocarbamate (ATC), O-alkyl-N-ethoxycarbonyl thiocarbamate (ECTC) and N-alkyl-N-ethoxycarbonyl thiourea (ECTU) was carried out by Sheridan et al. [67]. In this study, the flotation efficiency using an ATC collector was compared with the ECTC and ECTU collectors. The copper sample taken from an operating plant in South Africa contained mainly chalcocite with minor amounts of covellite and chalcopyrite. Pyrite was the undesired mineral. This ore contained 2% Cu, 5.5% S and 6.8% Fe. The effects of different process variables such as collector chain length (C2, C4 and C6); collector concentration (0.01, 0.025 and 0.01 mol/t) and type of frother (Methyl Isobutyl Carbinol, DF250 and Methyl Isobutyl Carbinol:DF250 in a 80:20 ratio) were analyzed. The optimum result in terms of copper recovery and grade was obtained for C4 ATC, i.e., a medium-chain length collector, which was corroborated with the investigation of Wang [68] that xanthate with a longer chain length produced a lower solubility compared to xanthate with two to five carbon atoms. The predicted optimum result revealed 97% copper recovery with 33% Cu grade using 0.09 mol/t of C4 ATC as the collector and a combination of DF250:MIBC as the frother in a 65:35 ratio. Thus, ATC was established as a suitable and potential collector for copper sulphide mineral flotation compared to ECTC and ECTU [68].

Hanson and Fuerstenau [69] studied the electrochemistry and wetting behavior of chalcocite using diethyl dithiophosphate and ethyl xanthate as the sulphide collector and also for chrysocolla using potassium salt of octyl hydroxamate as the oxide collector. It was also concluded that the selective separation of copper minerals (sulphides or oxides) is possible by carefully controlling the flotation pulp potential. The result confirmed the promising effect of hydroxamate as a collector for non-sulphide and oxidized copper ores without using a sulphidizing agent [70]. Author has summarized the common reagents used in copper sulphide flotation in Table 6.

**Table 6.** Common reagents for copper sulphide mineral flotation.

Ore	Collector	Frother	pH	Reference
Chalcopyrite	Sodiumisopropyl Xanthate (SIPX)	Polypropylene Glycol (Dowfroth 250; AR grade)	10.5	[62]
	Isopropyl ethyl thiocarbamate	Methyl Isobutyl Carbinol (MIBC)	6.3–5.1	[71]
	Sodium butyl xanthate (SBX)	Mixture of C5–C8 alcohol	8.0–8.5	[72]
	N-propyl-N-ethoxycarbonyl thiourea (PECTU)	Mixture of C5–C8 alcohol	8.5–9.0	
	Sodium ethyl xanthate (NaEX)	DowFroth 250		[73]
	Potassium amyl xanthate (PAX)	Methyl Isobutyl Carbinol (MIBC)	10.0–10.5	[74]
Bornite	<ul style="list-style-type: none"> <li>Di-ethyl dithiophosphate (di-C2-DTP) (Best)</li> <li>Di-ethyl-dithiocarbamate (di-C2-DTC)</li> <li>Ethyl Xanthate</li> </ul>	-	9	[65]
	<ul style="list-style-type: none"> <li>Potassium-Octyl Hydroxamate (Best)</li> <li>Ethyl Xanthate</li> <li>Di-ethyl dithiophosphate (di-C2-DTP)</li> </ul>	-	9.3	[75]
Chalcocite	<ul style="list-style-type: none"> <li>N-allyl-O-alkyl thionocarbamates (ATC)</li> <li>O-Alkyl-N-ethoxycarbonyl thionocarbamates (ECTC)</li> <li>N-alkyl-N-ethoxycarbonyl thiourea (ECTU)</li> </ul>	MIBC Polypropylene Dowfroth 250	9.4	[68]

In general, most of the copper deposits involve chalcopyrite as the major mineral, with the presence of other sulphide copper minerals (e.g., chalcocite and bornite) to different degrees. However, most of the reported studies are limited to a particular mineral,

and very limited studies have been focused on the mineral mixture. Additionally, there is a desire for further studies with a geo-metallurgical approach to understand floatability and kinetics.

## 6.2. Copper Oxide Minerals

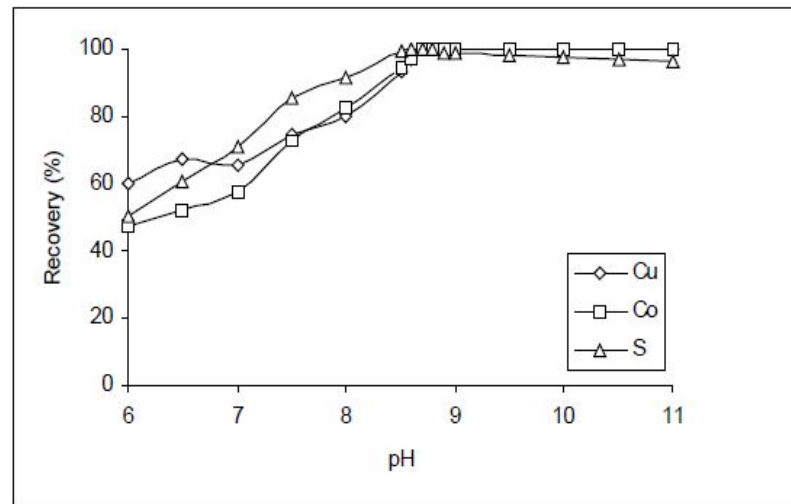
In general, sulphide copper ores have been beneficiated using flotation in an economic way, and the oxide minerals in the sulphide deposit are ignored because of their lower tenor and complexity in mineralogy [76]. The issue of the continual depletion of copper sulphide deposits shifted the focus of researchers to beneficiate the low-grade copper oxide deposit to meet its global market demand. Thus, copper oxide minerals also play a correspondingly important role in copper production [77]. Various copper oxide minerals often occur together in a deposit. They are generally found at a shallow depth of the Earth's crust, formed due to the weathering and oxidation of copper sulphide minerals [10,11]. The most often found copper oxide mineral is malachite ( $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ). The other oxide minerals are cuprite, azurite, chrysocolla, etc. Malachite with other copper oxide does not respond well to the conventional sulphide mineral collectors (e.g., xanthate), and therefore, alternative flotation approaches are needed.

Many researchers believe that the froth flotation of oxide copper ores is a complex method, and it needs the sulphidization stage. The oxide copper minerals have thick hydration film surfaces, which are hard to contact with air bubbles, implying that the flotation response of oxide is inferior to sulphide copper ores, technically and economically. Moreover, oxide copper ore enrichment with low dissolution rates generally utilizes [78]:

- (i) The froth flotation method after the sulphidization stage or
- (ii) The mixture of flotation and hydrometallurgy or
- (iii) Flotation segregation, whereas the hydrometallurgical route generally processes oxide copper ores with high dissolution rates.

Many researchers like Bulatovic have discussed a sulphidizing reagent for converting the oxide mineral surface to sulphide to behave as a sulphide mineral and respond to the sulphide collectors [79]. The efficiency of sulphidizing a reagent is highly dependent on its concentration. A strict regulation of collector dosage and control is mandatory in the plant—failing which, the flotation performance becomes poor [80–82].

Ziyadanogullari and Aydin studied the flotation of 40–45-year-old stockpiled ores from Ergani Copper Mining, Turkey, which were found not suitable for the recovery of the copper hydrometallurgical route [83]. They tried the flotation of such oxidized copper ore by introducing sulphidizing treatment, and hence, they were treated in a sulphurized medium containing different  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$  gases ratios. The feed contained pyrite, chalcopyrite and oxidized copper ore with 2.03% Cu and 3.73% sulphur. The flotation of a higher concentration of sulphurized sample gave approximately 100% recovery of copper and sulphur. The flotation result with potassium amyl xanthate as a collector and Dowfroth 250 as the frother at 8.7 pH produced 10% Cu with 100% recovery (Figure 13). During the sulphurization process, some composition alterations like degradation in the spinal structure, reduction of ions at higher state orders and differences in the crystalline structure took place. These modifications led to the formation of a sulphide compound and an increase in the degree of freedom. Thus, it was easier for the collector to get adsorbed by the sulphide compound to exert hydrophobicity and, finally, attach with the bubbles and float [83]. In the present investigation, the results can be compared with the conventional route to understand the potential of the sulphidization process. Additionally, the mechanical activation is another prominent area to alter the surface property in such cases that can help to generate a fresh surface to enable the better selectivity of reagents.



**Figure 13.** The flotation recovery of Cu, Co and S at different pH values (30.63 g H<sub>2</sub>S + 200.00 g H<sub>2</sub>O) [83].

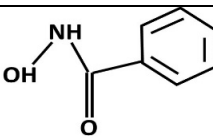
#### 6.2.1. Malachite

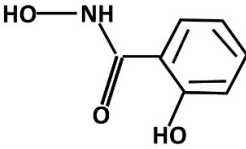
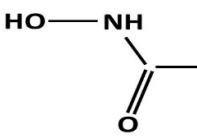
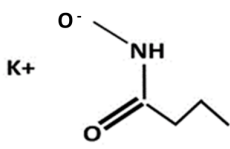
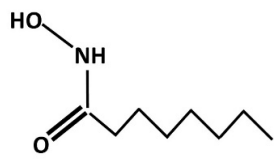
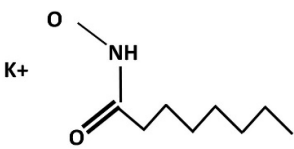

The most important industrially beneficiated copper oxide minerals are malachite (Cu% = 57.4) and azurite (Cu% = 55.2), whereas the least important minerals are chrysocolla (Cu% = 36.1) and cuprite (Cu% = 88.8%). In 1972, Glembotskii et al. [84] investigated the flotation of malachite and azurite by using the subsidization method. A feed with 1% copper was floated and concentrated with 80% recovery and 19% grade.

The effect of five alkyl hydroxamates (Aceto hydroxamate, K-butyl hydroxamate, octyl hydroxamate, K-octyl hydroxamate and tetradecyl hydroxamate) and two aromatic hydroxamates (benzo hydroxamate and salicyl hydroxamate) were studied on the flotation of the synthetic malachite-quartz ore mixture (Table 7). The zeta potential was taken into consideration to understand the reagent adsorption on the surface of the mineral. It showed that only benzo hydroxamate (aromatic) and octyl hydroxamate (alkyl) were productive in malachite recovery. Further, benzo hydroxamate was most selective, with a comparatively lesser concentration than octyl hydroxamate to get the same malachite recovery with slightly increased quartz, which corroborated the findings of Lee et al. [81] and Lee et al. [85].

The effective result on the recovery of oxide copper minerals like malachite and cuprite was reported by using alkyl hydroxamate as a collector, whereas finely disseminated cuprite and chrysocolla were not effectively floated with alkyl hydroxamate [85]. The direct recovery of copper oxide minerals with different oxyhydri collectors such as fatty acids, amine, phosphinic acids and hydroxamic acids [81,82,86–88] was investigated. Finally, hydroxamic acid was found to be effective in the recovery of malachite [79,81,85]. However, these findings have not been reconfirmed with real ore systems, which is still a challenging task.

**Table 7.** Hydroxamate collectors used in malachite flotation [89].

Hydroxamate	Abbreviation	Structure	Manufacturer
Benzo	BHA		Sigma Aldrich (St. Louis, MO, USA)

Salicyl	SHA		Alfa aesar (Haverhill, MA, USA)
Aceto	AHA		Alfa aesar (Haverhill, MA, USA)
K-Butyl	PBH		Synthesized
Octyl	OHA		Synthesized
K-Octyl	POH		Synthesized
Tetradecyl	THA		Synthesized

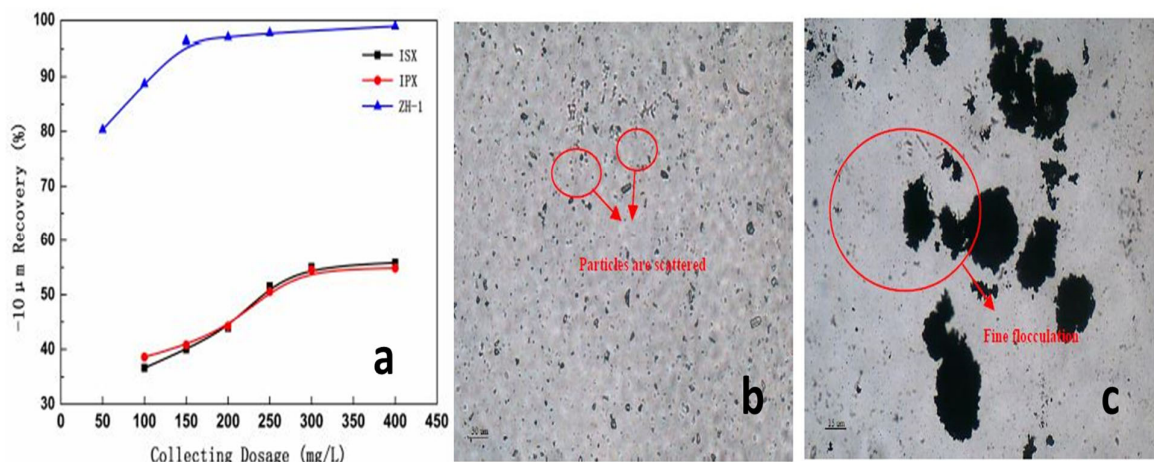
The effect of a chelating agent named KYL, consisting of improved ethylene phosphate used as an activator, for the flotation of copper oxide from Yongshan, Yunnan, was investigated by Yang et al. [88]. The ore contained 0.88% malachite and cuprite and 0.05% native copper. The sample was ground to 90% passing −200 mesh in the comminution circuit. Numerous flotation tests were conducted with sodium silicate, sodium sulphide and KYL as modifying agents, whereas xanthate and pine oil were used as the collector and frother, respectively. After four stages of rougher, a final concentrate of 22.87% copper grade was obtained with 83.99% recovery from the ore containing 0.55% total copper in the feed [90]. The performance of this study can be correlated and compared with the locked cycle test to understand its efficiency.

The interaction between malachite and sulphide ion species has been studied by an X-ray photoelectron spectroscopy analysis, zeta potential determination, surface adsorption and micro-flotation experimentation [91]. The result of the malachite recovery was interrelated with the contents of the sulphidization products and the residual sulphide ion species in the pulp phase. The sulphidization of malachite in Na<sub>2</sub>S solution resulted in the formation of copper sulphide species on the mineral surface with a negative charge. The concentration of cuprous sulphide increased with an increase in Na<sub>2</sub>S. The cuprous sulphide species product on the malachite surface resulted in cuprous monosulphide, cuprous disulphide and cuprous polysulphide. Disulphide and polysulphide, among them, play an active role in the sulphidization of the malachite surface. The increase in the

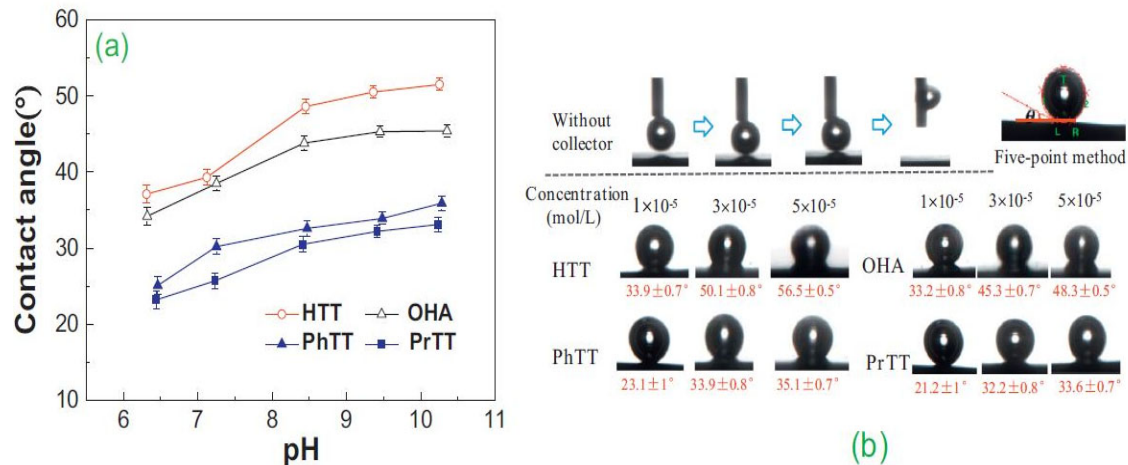
amount of  $\text{Na}_2\text{S}$  showed a detrimental effect on the malachite flotation. The decrease in recovery of malachite at a high concentration of  $\text{Na}_2\text{S}$  was attributed to the sulphide ion species remaining in the pulp phase leading to lesser collector adsorption on the sulphidized malachite surface. Therefore, a decrease in the malachite hydrophobicity was reduced [91].

Renfeng et al. [91] studied the effect of a new collector (ZH1, C3–5 carbon chain xanthate) for increasing copper oxide recovery, mainly fine-grained malachite ( $\sim 10\ \mu\text{m}$ ). A Pure copper sample (malachite and azurite) from the Dishui Copper Processing Plant of China was used in the flotation experiments. These researchers concluded a possible better recovery of malachite, using ZH1, which increased from 80 to 95%, by using isoamyl sodium xanthate (IPX) (Figure 14). Such a lower recovery by IPX was attributed to the fine particle size distribution of malachite particles. Due to the presence of a minor amount of alcohol in ZH1, it also produced some foam [92]. Hence it caused a sharp increase in the recovery of fine-grained malachite due to the rich bubble inclusions. ZH1 showed some flocculation quality due to which fine malachite could be flocculated to produce relatively coarse flocs to increase the probability of collision with the bubble and, thus, the better recovery of fine-grained particles [93,94].

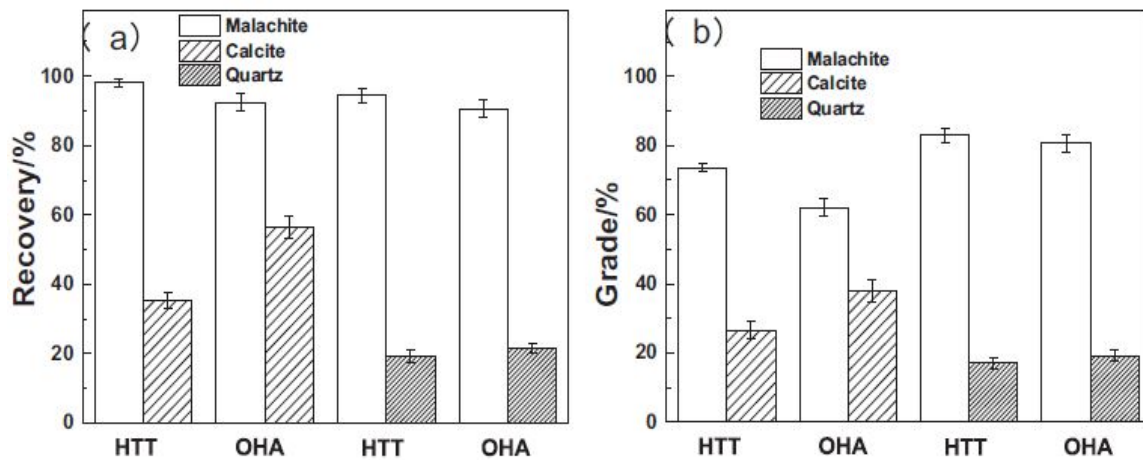
Liu et al. investigated the selective flotation of a copper oxide mineral (artificial mineral mixture) against quartz and calcite using three different types of synthesized Tetrazinan—a thione collector (HTT-6-hexyl-1,2,4,5-tetrazinan-3-thione, PrTT-6-propyl-1,2,4,5-tetrazinan-3-thione and PhTT-6-phenyl-1,2,4,5-tetrazinan-3-thione) and octyl Hydroxamic acid (OHA) [95]. Their order to impart hydrophobicity on the malachite surface was noted as follows:  $\text{HTT} > \text{OHA} > \text{PhTT} > \text{PrTT}$  (Figure 15). From their flotation results, it was observed that HTT results in relatively better and more selective flotation responses of malachite against gangue minerals (i.e., quartz and calcite) as compared to the other reagents (Figure 16). It is mainly due to the preferential adsorption of HTT on the malachite surface rather than quartz and calcite. Besides the longer heptyl group of OHA, HTT resulted in a higher recovery and grade of malachite versus quartz and calcite, which may be attributed to the formation of different bondings. Further, Liu et al. [96] developed a unique chelating collector named 5-(2,4,4-trimethylpentyl)-4-amino-1,2,4-triazolidine-3-thione (TMATT) for the improved separation of malachite from other gangue, and the flotation responses were compared with conventional OHA. Improved flotation responses were achieved by TMATT due to the stronger hydrophobization and higher selectivity against gangue [95].



**Figure 14.** (a) Relationship between the collector dosage and the recovery of fine-grained malachite. Distribution of malachite particles under the microscope (b) before and (c) after adding ZH-1 [91].



**Figure 15.** Bubble contact angle measurement of malachite surfaces as a function of different (a) pH and (b) collector dosages (HTT-6-hexyl-1,2,4,5-tetrazinan-3-thione, PrTT-6-propyl-1,2,4,5-tetrazinan-3-thione, PhTT-6-phenyl-1,2,4,5-tetrazinan-3-thione and OHA- octyl hydroxamic acid) [97].



**Figure 16.** Flotation recovery (a) and grade (b) of malachite in the presence of different reagents (under  $3 \times 10^{-5}$  mol·L<sup>-1</sup> HTT (6-hexyl-1,2,4,5-tetrazinan-3-thione) and octyl hydroxamic acid (OHA) at pH ~9.4) [97].

### 6.2.2. Chrysocolla

Chrysocolla is a copper silicate mineral that is nonresponsive to the sulphidizing process and responds poorly to sulphidization-xanthate flotation practice [98]. Laboratory tests have been carried out on the flotation of copper oxides, and it has been concluded that chrysocolla and malachite could be floated with a mercaptan collector. When a higher xanthate homolog (hexyl, dodecyl-Table 8) was used in large quantities, malachite particles floated. Chrysocolla particles remained unfloated. The addition of a mercaptan collector in the grinding mill resulted in superior recovery. A model was developed to attach mercaptan to the surface of chrysocolla, which included a reaction of mercaptan molecules with a copper oxide surface site. This reaction led to insoluble mercaptide and the splitting of a water molecule at the surface [99]. A new reagent was synthesized containing an aliphatic-aromatic structure, with a hydrocarbon chain and chelating group of an amino-thiophenol. It proved to be an effective collector for chrysocolla flotation in a pH range of 5.5–6. The infrared results showed that chelates of the amino-thiophenolate were formed on the chrysocolla surface under the best flotation conditions, which may have imparted hydrophobicity to the oxide mineral surface [100].



The flotation of oxide copper ore containing chrysocolla and quartz with 2.13% Cu was studied by Nagaraj and Somasundaran [100]. By using the collector emulsion containing 0.034 kg/t Tergitol and 0.5 kg/t LIX65N in hexane (3.0 kg/t), a concentrate was obtained within 4 min. of flotation and two stages of cleaning. The final concentrate contained 21.3% copper with 69% recovery [100].

### 6.2.3. Cuprite

The cuprite—type oxide copper from copper ore containing 1.29% Cu of Dishui Corporation, Xinjiang, China, was subjected to research work by Xiong et al. [101]. Sodium iso-amyl xanthate (SIAX) was used as the collector, sodium sulphide ( $\text{Na}_2\text{S}$ ) as the sulphidization reagent, methyl iso butyl carbinol (MIBC) as the frother and ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ) as the modifier. The results showed that ammonium sulphate is beneficial for the sulphidization of the copper oxide ore. At the optimum flotation conditions where 1000 g/t ( $\text{NH}_4)_2\text{SO}_4$ , 1000 g/t  $\text{Na}_2\text{S}$ , 800 g/t SIAX and 40 g/t pinitol oil were used, a copper concentrate with 18.23% copper grade and 73.46% recovery was obtained [101].

Han et.al. studied the surface sulphidization of cuprite mineral using  $\text{Na}_2\text{S}$  and concluded that the excessive quantity and/or dosage of a sulphidizer has a detrimental effect on the cuprite flotation activity [102]. Later on, they investigated the beneficial effect of pre-oxidation by  $\text{NaClO}$  (sodium hypochlorite) as an oxidant on the sulphidization of cuprite [103]. The direct sulphidization of the cuprite surface is ineffective because of its inherent hydrophilic nature. The oxidant helped in the transformation of the  $\text{Cu}_2\text{O}$  species ((Cu (I) low affinity towards sulphur ions) to  $\text{CuO}$  (Cu (II) active affinity towards sulphur ions) species, which enhanced the sulphidization process using  $\text{Na}_2\text{S}$ . Thus, higher flotation recovery was achieved using sodium butyl xanthate, which also corroborates Xiong and Zheng's results [72].

**Table 8.** Surfactants for copper oxide flotation.

Ore Mineral; Gangue Mineral	Sample Source (Ore Deposit/Country)	Collector	Remarks	References
Malachite; Quartz	AMR Mineral and Metal Inc., Canada	Benzo Hydroxamate[Best] Salicyl Hydroxamate Aceto Hydroxamate K-butyl hydroxamate Octyl Hydroxamate K-octyl Hydroxamate Tetradecyl Hydroxamate	Synthesized ore (mixture of malachite and quartz)	[89]
Chrysocolla; Quartz	Miami, Arizona	Hexyl Mercaptan, Dodecyl Mercaptan (Higher Xanthate)	Natural Ore	[99]
	Miami, Arizona	Aminothiophenol	Natural Ore	[98]
Cuprite; Quartz, calcite	Copper Company of Dishui Corpora- tion, Xinjiang, China.	Sodium Iso amyl Xanthate (SIAX)	Natural Ore	[104]
Cu Sulphide (Chalcopyrite and bornite) and Cu Oxide (Malachite with small Azurite); Quartz	Sherwood Copper's Minto mines, Canada	N-octyl hydroxamate (AM28)	Synthesized ore (Mixture of Cu Sulphide Cu Ox- ide:::(70:30))	[81]

### 6.3. Mixed Copper Ore

Rule investigated an ore containing 1.77% total copper (1.67% and 0.1% as copper oxide and copper sulphide, respectively). Mineralogically, the ore contained 80% of the minerals atacamite and paracamite. The ore sample was ground to 97%, passing 150  $\mu\text{m}$ , and all flotation experiments were performed at pH 8.7. A mixture of potassium octyl hydroxamate (0.2 kg/t) and potassium amyl xanthate (0.4 kg/t) was added as the collector and conditioned for 20 min. After the addition of pine oil and methyl iso butyl Carbinol mixture in a 1:1 ratio (as a frother), a copper concentrate of 83.6% recovery with a copper

grade of 6.88% (6.52% copper oxide and 0.36% copper sulphide) was obtained [105]. However, the kinetics data of each type of mineral were not evaluated, which is critical in designing the reagent suite, along with the conditions needed for better collector adsorption. Additionally, the liberation and particle size distribution of each type of minerals are critical in analyzing the floatability aspects.

The copper oxide deposit of Dali in Yunnan, China, contained 0.69% Cu (0.46% and 0.23% in the form of sulphide and oxide minerals of copper, respectively) and 11.24 g/t silver. The ore was upgraded by the sulphidization process, followed by xanthate collector flotation. Sodium sulphide as a sulphidization agent (100 g/t) and butyl xanthate and ammonium dibutyl dithiophosphate as a combined collector were used during the experiments. Applying closed-circuit tests, a copper concentrate with 18.34% copper grade and 70.13% copper recovery was obtained [106]. A mineralogical study also revealed the presence of chalcopyrite, malachite and chrysocolla as major copper minerals with minor amounts of chalcocite, bornite and covellite in the beneficiation of copper oxide ore from Yunnan [106]. The best test conditions were determined as 1000 g/t, 1000 g/t, 150 g/t and 30 g/t of lime, sodium sulphide, sodium n-butyl xanthate and terpenic oil, respectively. Even though it was a mixed ore, the focus was on the flotation of sulphide minerals. Finally, after closed-circuit tests of two roughing, two cleanings and one scavenging, a concentrate containing 20.20% Cu with 68.11% recovery was obtained [106].

The recovery of copper from the Abu-Swayel ore deposit by reverse flotation was attempted by Abdel-Hady and his co-researchers [107]. The deposit contained mainly copper oxide minerals, i.e., malachite, calcanthite and brochantite, which show a poor response towards flotation. The other minor associated minerals were chalcopyrite, bravoite, violarite, hematite, goethite and ilmenite. The reverse flotation tests were carried out using oleic acid as the collector and pine oil as the frother to retain copper oxide minerals in the pulp. The results showed that about 90% copper recovery with 10% copper grade could be achieved by using a 1.5 kg/t oleic acid collector at pH = 10, 7 dm<sup>3</sup>/min air flow rate and 5 min flotation time. The copper mineral lost in the froth product may be recovered by cleaning of the concentrate under the same flotation conditions [107].

A flotation study was carried out on a low-grade complex copper ore sample by Singh and his co-researcher [108]. The sample was of low grade, with a copper content of 0.95% and silica and alumina as the major impurities. The primary copper-bearing mineral was chalcopyrite, followed by bornite and covellite, with tetrahedrite, malachite and azurite. The flotation tests were carried out using sodium iso propyl xanthate (SIPX) as the collector for the sulphide mineral, methyl isobutyl carbinol (MIBC) as the frother, sodium hydroxide as the pH regulator and sodium sulphide as the sulphidizing agent. The presence of oxidized copper minerals and slimes considerably affected the flotation performance. However, the use of sulphidizing agent helped to enhance the copper recovery by converting the surface of oxide minerals into sulphide and providing it as suitable for flotation using xanthate. The use of sodium silicate as a depressant for siliceous gangue can also improve the copper grade. After rougher flotation followed by two cleaning stages, a copper concentrate with 29.25% Cu at 81.7% recovery was obtained.

A patentable work was done on a Chilean copper oxide sample, which had a grade of 2.6% copper oxide and 0.28% copper sulphur. The sample was ground to 60%, passing 75 µm. The reagents used in the tests were potassium amyl xanthate (PAX), pine oil, sodium sulphide, 5-methyl benzotriazole, light oil and mobile oil no. 20. Finally, a flotation concentrate with 27.8% Cu grade and 71.2% recovery was obtained [109].

A synthetic mixed copper sample was studied by blending 70% sulphide copper and 30% oxide copper from Sherwood Copper's Minto Mine Yukon in Canada with a grade of 3.6% Cu. Potassium amyl xanthate (PAX) and potassium n-octyl hydroxamate (AM28) were also used as the collectors. The sulphidization reagent, i.e., sodium hydrogen sulphide (NaHS), was used to modify the oxide surface. The dosages of AM28 and MIBC were maintained at 1200 g/t and 50 g/t, respectively. In the cleaning stages, an extra 100 g/t of AM28 and 50 g/t of MIBC were added. This process yielded a concentrate assaying

33.9% copper with 78.5% recovery. It was concluded that AM28 successfully beneficiated malachite and minor azurite in Minto's oxide ore [71,81].

To develop a flotation procedure for an oxide copper ore, samples from a region of Central Africa were subjected to flotation tests [110]. The feed grade of 4.5% Cu was contributed by 88% copper oxide minerals and 12% sulphide minerals. A concentrate of 18% Cu grade was obtained with potassium amyl xanthate as the sulphide collector; n-octyl hydroxamate, Oleofloat 6540, rinka lore, diesel, sodium carbonate and tall oil as the oxide collectors; sodium hydrogen sulphide (NaHS) as the sulphidizer and Dowfroth 200 as the frother. The recoveries achieved from the experiments were less than 50%, despite trials with varying reagent combinations and conditions. The poor recoveries were attributed to copper silicates around 70% by mass, which made it too complex to be floated by the conventional method. The sulphidization procedure at a high flotation temperature and extended flotation residence time could give the best results [110]. Similarly, an experimental research work was reported on an oxide copper ore from Guizhou, China. The ore contained 1.15% Cu with chalcopryrite, chalcocite, covellite and bornite as the sulphide minerals and malachite and chrysocolla as the oxide minerals, whereas quartz, dolomite and mica were the main gangue minerals. Using a new collector, in a closed-circuit flotation, a concentrate of 22.1% Cu grade with 88.52% recovery was reported [110].

Due to the presence of higher oxidized and carbonaceous mud, traditional flotation resulted in the poor recovery of copper from copper–cobalt sulphide–oxide mixed ores [111]. Before the direct flotation of these types of ores, desliming and decarbonization were suggested via the flotation process, using alcohol pine oil, alcohol butyl ether and an oil combined with a frother. The used frother showed a significant result in terms of desliming and selective copper flotation. After that, the sample was subjected to copper oxide activation, using both sodium sulphide ( $\text{Na}_2\text{S}$ ) and sodium hydroxide sulphide (NaHS). Amyl xanthate was used as a collector at rougher, cleaner and the scavenging stages. A concentrate with 21.2% copper grade was obtained with 88.55% copper recovery from the sample, containing 2.63% Cu and 0.04% Co [111].

The copper oxide ore of the Yangla Mine in Yunnan, China, with 1.02% copper was subjected to flotation with a mixture of potassium amyl xanthate (PAX) and hydroxamate AM28 as the collector. A rougher concentrate was reported with a 3.19% Cu grade and 38.4% recovery [112]. Another flotation study was carried out on copper oxide ore from Yunnan, China, containing covellite, malachite and bornite as copper minerals and quartzite, dolomite, plagioclase, chlorite, calcite, hematite and pyrite as major gangue minerals. With a reagent combination of butyl xanthate as the collector, pine oil as the frother, sodium sulphide as the sulphidizing agent and lime as the pH regulator, after three stages of cleaning, a concentrate with 18.06% copper and 80.81% recovery was reported [77].

Ausmelt developed an important hydroxamate, i.e., AM28 (potassium n-octyl hydroxamate). It has been implemented in flotation and has been found as an effective collector for oxide copper minerals and native copper over a wide pH range. It is also confirmed as an efficient collector for chrysocolla in an alkaline pH range, i.e., pH 7–10 [113]. Mexican mixed-type copper ore contained ramsbeckite and malachite as the copper oxide minerals and chalcopryrite as the copper sulphide mineral, with  $\text{SiO}_2$  as the main gangue mineral. The total copper assay was 1.19%—out of which, oxide copper was 0.84% and sulphide copper was 0.35%. The combination of flotation and leaching were studied. Using sodium sulphide and butyl xanthate, a concentrate with 19.01% copper grade and 35.02% recovery was obtained. Around 83.33% oxide copper was recovered from the tailing via the leaching method under suitable conditions stirring for 1 h at 25 °C with a mixing speed of 500 rpm, 1 M  $\text{H}_2\text{SO}_4$  and mass ratio (slurry/liquid) of 3. A final yield of 89.18% was obtained after the completion of flotation and leaching, which was better than the single leaching or flotation technique. It was concluded that a combination of flotation and leaching was convenient for the beneficiation of Mexican mixed copper ore. Hence,

the “flotation-agitation-leaching-solvent extraction-electro-winning” process route was able to produce a pure copper of 99.9% [114].

A bench-scale test on the beneficiation of mixed oxide–sulphide ore of copper from the Malankhand deposit was studied. The effect of sodium isopropyl xanthate (SIPX) and sodium diethyl dithiocarbamate (DTC) as collectors; sodium silicate, guar gum, Mangnafloc-140 and Mangnafloc-351 as depressants and pine oil as the frother were systematically studied and optimized. The improved result was obtained with SIPX and sodium silicate at pH 9. The results obtained from dithiocarbamate were quite good compared to SIPX, but it has not been reported in the literature about their industrial-scale application [115]. For better understanding the reagent suite to float the mixed ore, a detailed list of used reagents, along with the case details, is summarized in Table 9. From Table 9, it can be found that Potassium octyl hydroxamate (POH), Potassium Amyl Xanthate (PAX) and Sodium Iso-propyl Xanthate (SIPX) have been used at different proportions to float the copper minerals effectively from the mixed ore. The commonly used frother is MIBC or a mixture of IMPC and pine oil. Additionally, surface modifiers in the form of sulphidizers such as Na<sub>2</sub>S and (NaSH) have been used to enhance the flotation selectivity. There is enough scope to study the reagent chemistry and their synergistic effects on the mixed ore’s floatability.

**Table 9.** Reagents for the mixed copper ore (sulphide and oxide).

Ore	Deposit /Country	Collector	Frother	Modifier	Remark	Reference
Atacamite + paracamite + chalcopyrite	Hanna Mining Company, Ohio.	Potassium octyl hydroxamate (POH): Potassium Amyl Xanthate (PAX): 1:2	Pine Oil: MIBC: 1:1	-	Patentable work for the effective flotation of mixed copper ore using hydroxamate collector	[104]
Chalcopyrite ([major] + Malachite, Azurite (traces)	Indian copper mine	Sodium Iso Propyl Xanthate (SIPX) Potassium Octyl hydroxamate (POH)	MIBC	NaOH (Ph), Na <sub>2</sub> S (Sulphidizer) and Na <sub>2</sub> SiO <sub>3</sub> (Depressant)	Single Rougher step followed by three stage cleaning yield final concentrate of 31.77% Cu from 0.95% Cu feed	[109]
Sulphide (Bornite + Chalcopyrite) and Oxide (Malachite + Azurite)	Sherwood Copper’s Minto mines, Canada	Potassium Amyl Xanthate (PAX) + Potassium n-octyl hydroxamate (AM28)	MIBC	Sulphidizer (NaHS)	AM28 recovered copper oxide mineral without affecting recovery of sulphide minerals	[116]
(Cu Oxide (88%) + Cu Sulphide (12%))	Central Africa	Potassium amyl Xanthate (PAX)- Sulphide collector N-Octyl hydroxamate and Oleofloat 6540-Oxide collector	Dowfroth 200	Sulphidizer (NaHS)	Mixed natural ore	[116]
Copper Mixed ore (Chalcopyrite + Malachite)	Malankhand copper mine, India	Sodium Iso-propyl Xanthate (SIPX) Sodium Diethyldithiocarbamate (SDTC)	Pine Oil	Sodium Silicate	Only copper sulphide recovery is focused even after its mixed type	[115]

#### 6.4. Effect of Mineralogy on Copper Mineral Zeta Potential

In colloidal chemistry, the zeta potential is used to study the characteristics of minerals in a liquid dispersive system. Thus, it plays an important role in the physicochemical separation processes, i.e., flotation and flocculation. The relation between mineral electrochemistry and the practice of flotation has been extensively discussed for decades [117–120]. The zeta potential value remains positive for pH lower than the IEP and vice versa. IEP is defined as the pH, where the net charge on the mineral surface is zero. According to Ottewill, the aggregation tendency of mineral particles is dominant within −30 mV to +30 mV zeta potential [121], which was later confirmed by Mokone et al. [122] and also ascribed that copper sulphide mineral in suspension was found to be stable at a more negative zeta potential. It was also explained that, at the IEP, the colloidal system is least stable (i.e., aggregation of the copper mineral particle is confirmed and, hence, affects the

flotation process). Mineralogical association of an ore mainly controls the colloidal system's pH, adsorption of the reagent on the mineral surface and, ultimately, zeta potential, which is responsible for effective flotation.

From the literature, it was found that Malanjkhand chalcopyrite has a positive zeta potential up to its isoelectric point, which was found to be <3 pH [123]. The same IEP of chalcopyrite was previously reported by many researchers [43,124,125]. The IEP of pure chalcopyrite was reported around a pH of 5.7 [68,78]. The shifting of IEP towards a lower pH was due to the presence of a higher amount of quartz in Malanjkhand copper, whose IEP was at a pH of 2, as per the previous literature [126]. Copper sulphide minerals are oxidized easily due to their surface reactive nature, and their order of oxidation is given as follows [127]: Chalcocite > Tennantite > Enargite > Bornite > Covellite > Chalcopyrite. The IEP of high-purity malachite was reported at a pH of 8.4 [128], which was nearer to the IEP value reported by Liu et al. [129,130]. Li et al. [130] studied the adsorption mechanism of the chelating reagent on the surface of the malachite mineral from the Lupe Mine in Mexico. During this investigation, the IEP of the malachite ore (in the absence of the reagent) was found at a pH of 9.1, which corroborates with the findings of Liu et al. [129] (i.e., at a pH of 8.7). The slight change in the IEP (from pH 8.7 to 9.1) may be due to pseudo malachite in the Lupe Mine deposit. Many other authors have outlined that chrysocolla has no IEP [131,132], whereas a researcher informed the IEP of chrysocolla at pH 2 and pH 6.5 [133]. The varying IEP values of chrysocolla may be reflected due to the variability in its mineralogical composition. Based on the above literature, the optimum pH ranges reported as the IEP for different copper minerals are listed in Table 10. It is concluded that the oxidation of copper sulphide minerals is confirmed by the zeta potential analysis. Its variation (zeta potential value) with respect to the pH reveals the extensive presence of a copper hydroxide layer covering the sulphur-rich surface, which is responsible for escalating the oxidation environment. From Table 10, it is also found that chalcopyrite can be present at a lower IEP, which may be due to the presence of silicate gangue minerals, along with the ore. Similarly, the malachite is present at a higher range of IEP (8.4–9.1). In this direction, detailed studies are necessary to analyze the surface charge of the mixed ores, as well as their surface oxidation.

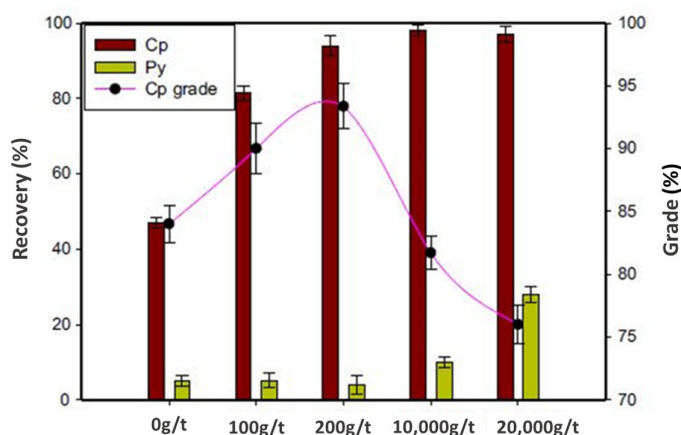
**Table 10.** Iso Electric Points (IEP) of different copper minerals.

Mineral	Ore Deposit	IEP (at pH)	Remark	Reference
Chalcopyrite	Malanjkhand Copper Mine, India	2.9–3.3	Lower IEP is due to the presence of abundant silicate gangue	[43,124,125]
Malachite	Guangxi Province, China	8.4–8.7	High purity mineral	[128–130]
	Lupe Mine, Mexico	9.1	Presence of Pseudo malachite (5%)	[134]
Chrysocolla	Dongchuan, Yunnan Province, China	Not found	Pure Mineral with 40% SiO <sub>2</sub>	[131]
	Exotica Mine, Chile	Not found	Purest Lump with 43% SiO <sub>2</sub>	[132]

#### 6.5. Bio-Collector for the Flotation of Copper

Thiol collectors (e.g., xanthate, thionocarbamate and dithiophosphate) are extensively used as reagents for the flotation of copper minerals. These “sulphur”-based collectors are costly and can produce toxicity with an abhorrent odor [69,78]. The use of xanthate can cause a detrimental effect on health and the environment, as it is highly inflammable and emits virulent carbon disulphide (CS<sub>2</sub>) gas during its production [135,136]. Moreover, in 1998, Boening also stated that xanthates are dangerous for aquatic habitats [137]. These drawbacks lead to the emergence of alternative flotation reagents to xanthate for copper sulphide minerals with a higher selectivity and eco-friendly nature. Bauer et al. [138] and Green et al. [139] had patented the recovery of chalcopyrite from a feed containing 0.58% Cu, using different oils as a collector, in a replacement for the thiol collector (thio phosphate). The flotation result produced a concentrate of grade 8.43% Cu with 82% recovery.

Owusu and his co-researcher studied the selective flotation of chalcopyrite from pyrite using fatty acid-based oils such as canola oil and palm oil instead of sodium isopropyl xanthate [140]. The flotation results showed an improved Cu recovery and grade when 200 g/t canola oil was used (Figure 17). Thiol based collectors are widely used in copper mineral flotation, mainly due to their high potential towards selective flotation, lower prices and easy availability. However, many researchers have shifted their focus towards bio-collector flotation, where fatty acid-based oils (canola oil/palm oil) are used as a substitute to the conventional sulphhydryl collector for the recovery of sulphide copper minerals. Bio-collectors have yet to prove their applicability with the ore variations. Additionally, there is not much literature on the variations in the temperature of the slurry, which is very critical in plant operations.



**Figure 17.** Chalcopyrite and pyrite recoveries, as well as chalcopyrite grade data, as a function of canola oil dosage for a 50:50 chalcopyrite–pyrite mixture [140].

#### 6.6. Effect of Water Quality on Copper Flotation

Many researchers have investigated the water quality in copper flotation [141–144]. According to Alvarez and Castro, pure chalcopyrite's flotation performance is affected by using sea water [141]. Castro also reconfirmed this observation; the deleterious effect was observed in chalcocite flotation [141,142]. Bakalarz et al. studied the effect of varying quality water (i.e., natural saline water, saline + tap water, saline +NaCl and tap water) on copper flotation [145]. They concluded that the dilution of tap water with saline water in a ratio of 70:30 produced a better copper flotation response as compared to the other water samples (Figure 18). Smith and Heyes investigated chalcopyrite-bornite ore's flotation and reported that chalcopyrite recovery is not enhanced by using seawater, while the flotation kinetics moderately improve. On the other hand, bornite recovery was diminished due to the entrainment [143].



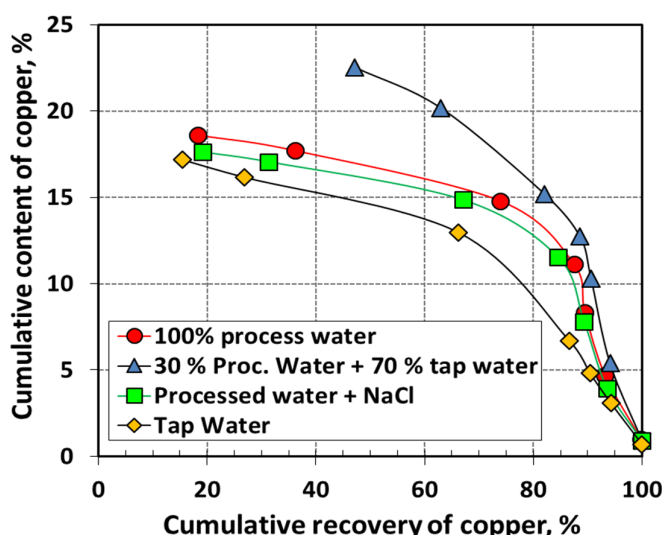


Figure 18. Result of the copper ore flotation response in different water types [145].

### 7. Problems Associated with Copper Tailings

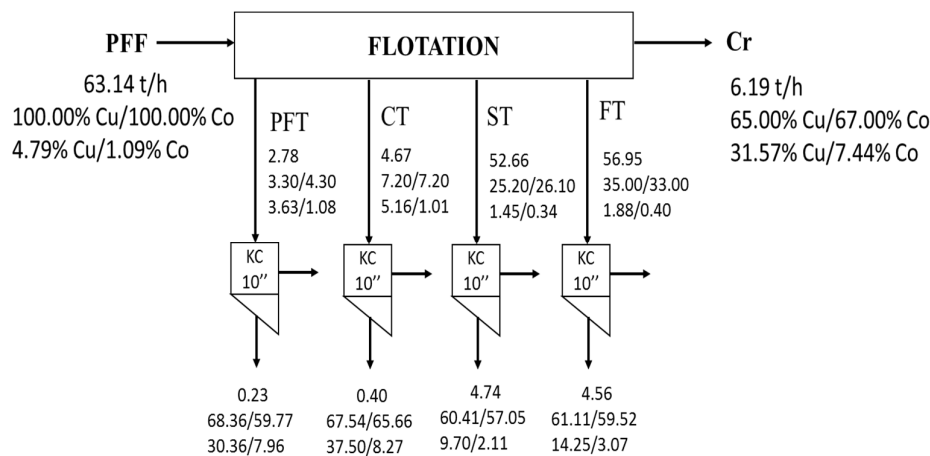
Currently, the mining sector has encountered problems related to off-grade copper deposits, while their demand in the global market has hiked [146]. Hence, tailing dams are considered as a potential secondary source to meet the requirements. Falagan et al. [147] stated that the past beneficiation techniques are less efficient in processing tailing. Since 1960, the copper grade of tailing dams has decreased from 0.74 to 0.14% [148], and the past tailing ponds consist of a higher grade compared to the current deposits. Therefore, their reprocessing is profitable to the industry in various ways. The processing of tailings is not only cost-effective; it also reduces the environmental pollution [18,149–151].

A number of studies were focused on the recovery of copper from its flotation tailings [18,22,152]. Ramakokovhu et al. [22] investigated the beneficiation of copper tailings from the Konkola Copper mine in Nchanga, Zambia. They studied the leaching characteristics of copper tailing before and after upgrading by using a Knelson gravity concentrator. The raw tailing contained 0.61% Cu, which was upgraded to 1.2% Cu after physical treatment with Knelson (Table 11).

Table 11. Elemental composition of the raw tailing feed and upgraded feed [22].

Stream	Element (Wt.%)				
	Cu	Fe	Al	Mg	O
Raw tailing feed	0.61	2.44	9.17	3.42	50.16
Upgraded feed	1.02	1.64	6.54	1.52	54.97

Katwika et al. reprocessed copper–cobalt tailing from the New Concentrator of Kipushi using a Knelson gravity separator. Due to the copper–cobalt fine dissemination in the gangue matrix, a traditional gravity unit may not be effective. The copper tailing was upgraded to 31.57% Cu and 7.44% Co, with recoveries around 65% Cu and 67% Co, respectively (Figure 19) [20]. Continuous depletion of high-grade copper ore deposit has constrained us to utilize the old tailings as a secondary resource. Numerous copper tailing beneficiation studies have been reported in the literature using a Knelson gravity separation as a preconcentration due to the liberation of copper mineral at a very finer-sized fraction where studies with a falcon gravity separator are limited. Apart from these methods, selective reagent combinations may be practiced in flocc-flotation methods for the recovery of finely disseminated copper sulphide minerals.

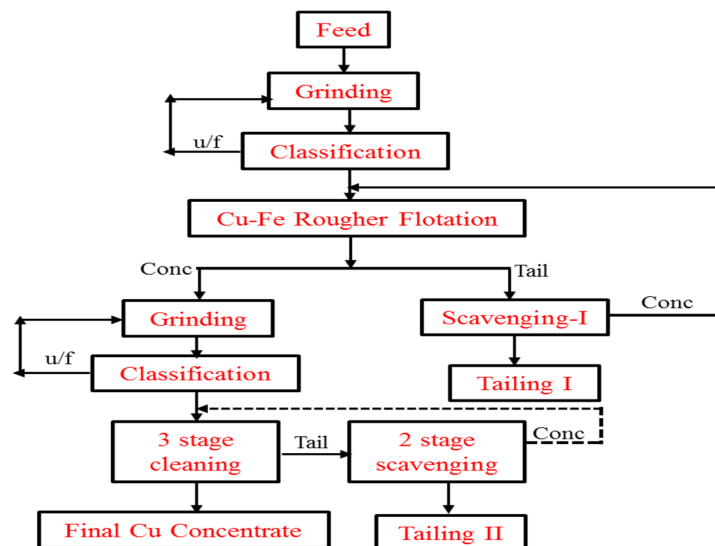


**Figure 19.** Schematic for the separate treatment of tailings (PFF: Pre-floated feed, PFT: Pre-float tails, CT: cleaning tails, ST: scavenger tails and FT: final tails) [20].

## 8. Different Aspects of Copper Plant Flowsheet/Practice

### 8.1. Dexing Copper Plant, China

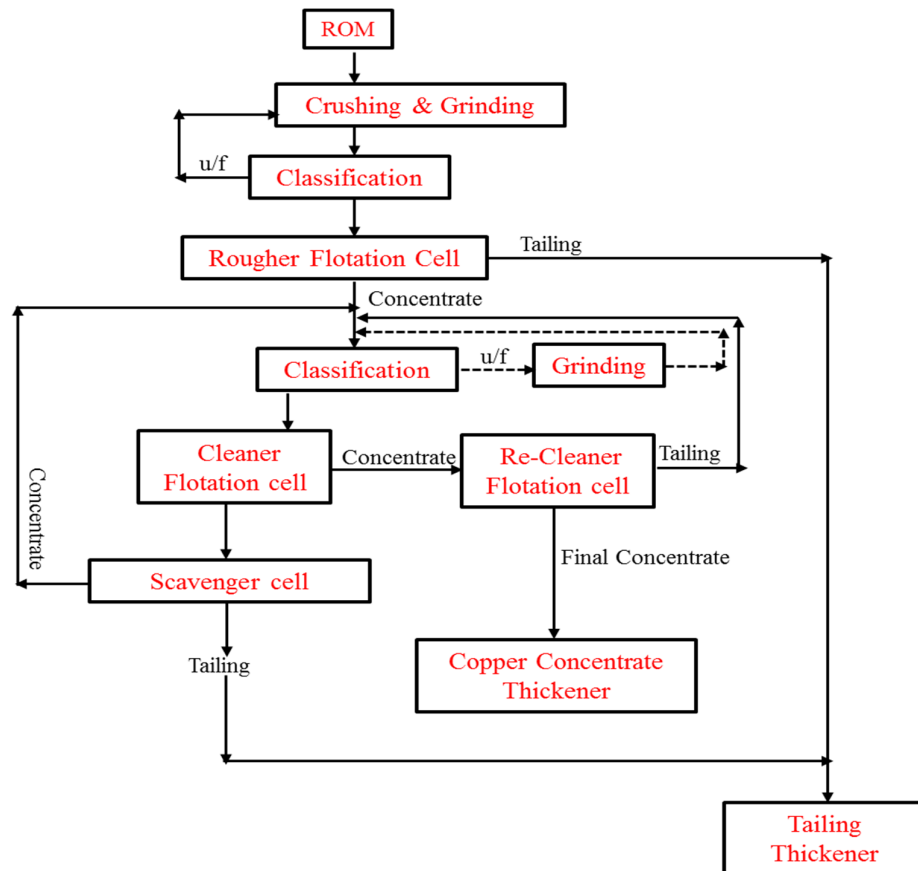
A refractory copper porphyry ore was investigated through both bench-scale and industrial-scale flotation experiments to concentrate copper minerals at the Dexing Copper Mine of Jiangxi Province in China by using N-propyl-N-ethoxycarbonyl thiourea (PECTU) and sodium butyl xanthate (SBX) as the collectors (Figure 20). They observed that PECTU has a strong collecting power for copper sulphide minerals and enhanced selectivity against iron sulphide minerals under moderately alkaline conditions. A combination of PECTU and SBX resulted in an increase in the Cu grade (from 0.44 to 23.16%), with 75.6% copper recovery in the final concentrate, whereas single SBX produced a final concentrate with a 22.23% Cu assay and 74.57% copper recovery. It also provided a better flotation separation of Cu/Fe sulphide minerals at a pH of 10.5 with comparatively less lime addition. The reasons for the better flotation performance of PECTU have been explained, as it had a moderate electron-donating power, and, also, the covalent bond's energy between PECTU and iron sulphide minerals may be low enough to improve its non-selectivity for iron sulphide minerals [71].



**Figure 20.** The flow sheet of bulk flotation by separation in the Dexing Copper Mine [71].

### 8.2. Sungun Copper Plant, Iran

The combined effect of four flotation reagents, i.e., Z11 (sodium iso-propyl xanthate) and AP407 (combination of mercapto benzothiazole and dithiophosphate) as the collectors and AF56 (ether polyglycol) and AF70 (Methyl Isobutyl Carbionl) as the frothers were evaluated by Vazifeh et al. [153] using a statistical technique in the rougher concentrate plant of Sungun Copper in Iran (Figure 21). The feed contains mainly chalcopyrite, chalcocite and covellite with 0.61% Cu. Two levels of a four-factorial design were used for the modeling and optimization of these flotation reagents. The high correlation coefficients of the model equations for the grade ( $R^2 = 0.89$ ) and recovery ( $R^2 = 0.96$ ) indicated that the predicted values were in good coordination with the observed values. With using the optimum dosage of reagents, it was possible to produce a concentrate of maximum copper recovery and grade [153].



**Figure 21.** Flow sheet of the Sungun Copper Flotation plant [153].

### 8.3. Telfer Copper Processing Plant, Western Australia

Seaman et al. studied the upgrade of the Telfer copper processing plant in Western Australia by adding new cleaning and regrinding circuits [153]. Previously, the copper minerals were initially recovered, followed by pyrite (Figure 22). After reopening in 2004, it has faced many challenges, as a low-grade copper concentrate was produced due to the uncontrolled entrainment of non-sulphide gangue. Thus, they have modified the existing circuit by installing two ISAMill for ultrafine grinding (for the copper and pyrite flotation circuit), two Jameson cells for enhancement of the fine gangue rejection and a bank of five Outotec flotation cells for the recovery of copper and gold from the pyrite reground stream (Figure 23) [154].

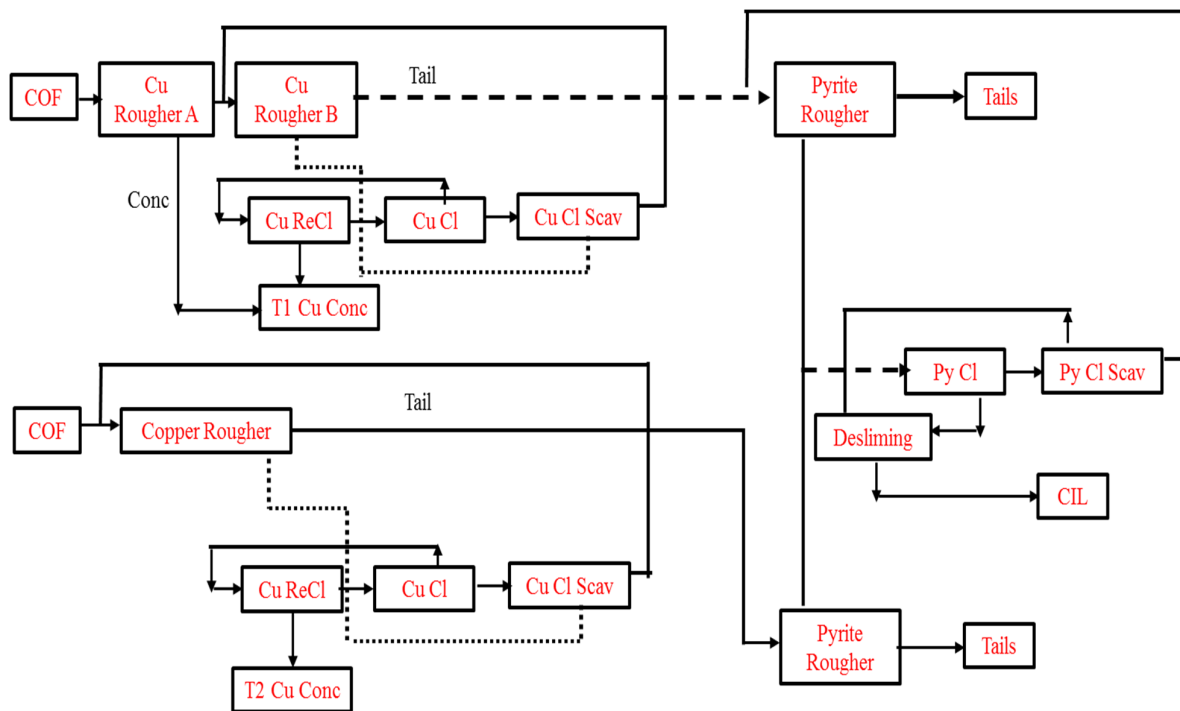


Figure 22. Pre-configuration plant flow sheet of Telfer [154].

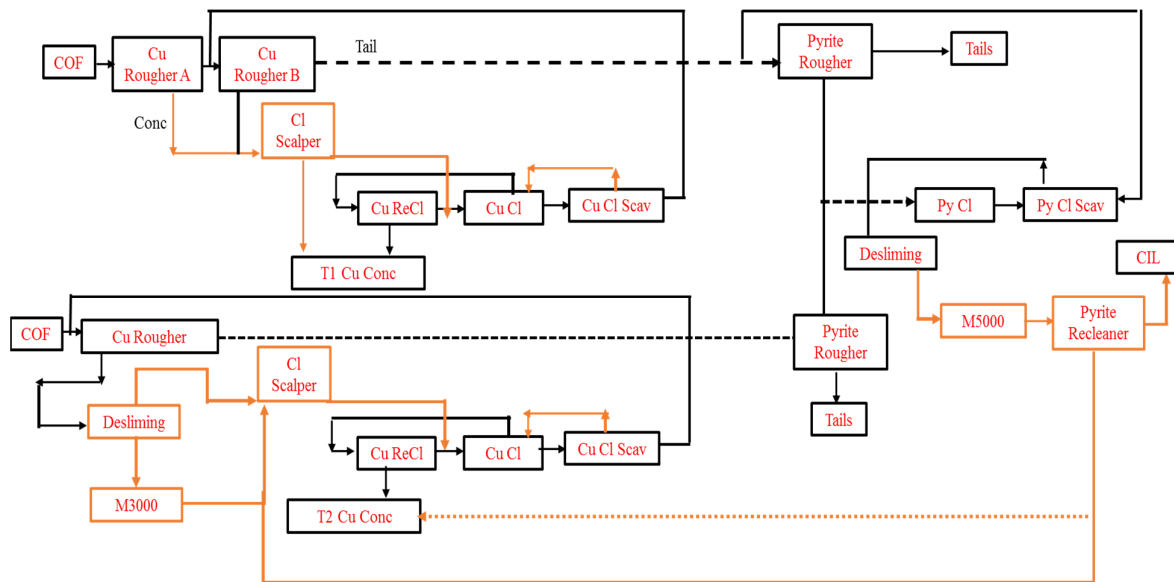


Figure 23. Post-configuration plant flow sheet of Telfer [155].

#### 8.4. Mosabani and Malanjhand Copper Plant, India

Sastri et al. explained the copper plant flow sheet of the Mosabani and Malanjhand copper mines, India [156]. The ROM grade of the Mosabani copper plant (Figure 24) is around 1.5% Cu and crushed in a close circuit (by two parallel jaw crushers, screening and then the screen's overflow was further crushed in a cone crusher). The products were subjected to ball mill operation in a closed circuit with the spiral classifier. The classifier's overflow was fed into the flotation circuits, with SIPX as the collector, pine oil as the frother and soda ash as the pH regulator. The final concentrate obtained from flotation cells with a higher grade (25% Cu) were filtered in a vacuum disc filter. The final tailings

with 0.05% Cu were dumped in the tailings dam. The ROM of the Malanjkhand copper plant (1.2% Cu) (Figure 25) was the feed for the closed-circuit crushing unit (gyratory crusher-screen-secondary crusher-screen-tertiary crusher), and the products were transferred into the ball milling unit in the closed circuit with hydrocyclone. The overflow of hydrocyclone was sent to the flotation circuit units. A vacuum disc filter sorted the final concentrate obtained from the second stage cleaner with a high-grade copper content (25% Cu). Similarly, the final tailings of 0.08% Cu were discarded into the tailing dam.

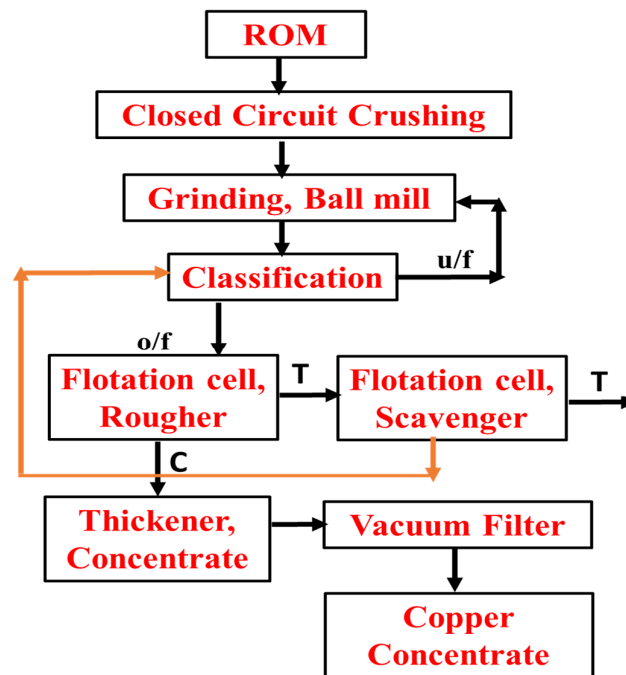


Figure 24. Mosabani copper concentrator plant flow sheet (India) [156].

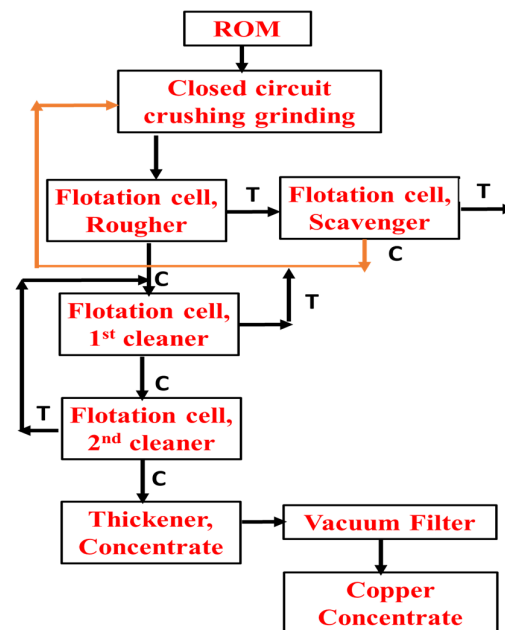


Figure 25. Malanjkhand copper concentrator plant flow sheet (India) [156].

### 8.5. Cerro de Maimón Copper Plant, Dominican Republic

The Cerro de Maimón deposit's mineralogical analysis confirms the presence of chalcopyrite, pyrite and sphalerite as the major minerals, along with covellite, bornite and chalcocite. There are two different plants, a sulphide plant (recovery of copper and zinc) and oxide plant (recovery of gold and silver) [157]. In the sulphide plant (Figure 26), the feed content was 2.7% Cu. The feed ROM was subjected to primary grinding followed by rougher flotation. The concentrate obtained was sent to the regrinding circuit, followed by cleaner flotation. The tailings, i.e., rougher flotation and cleaner flotation, were taken into another flotation circuit to recover zinc as a coproduct. The final cleaner stage produced a concentrate with 28% Cu at 83.3% recovery (Table 12).

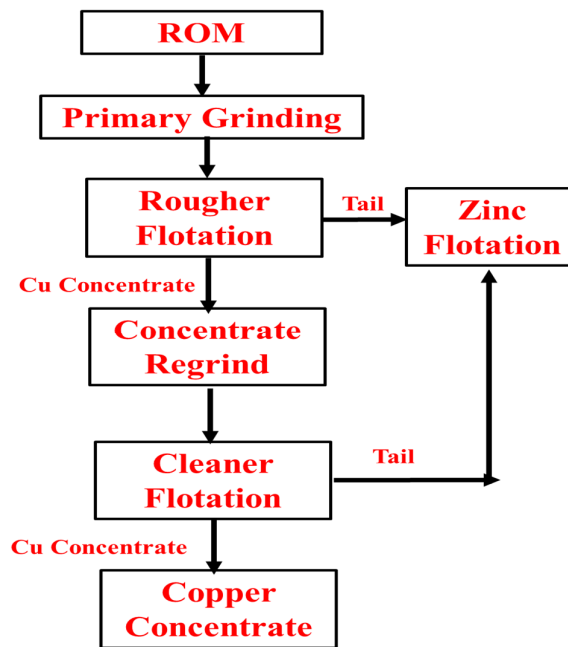


Figure 26. Flow sheet of the Cerro de Maimón copper plant (Dominican Republic) [157].

Table 12. Summary of the copper plant flow sheets.

Sl. No.	Mineralogy	Place and Country	Cu <sub>FG</sub> (%)	CCG; Cu <sub>CR</sub> (%)	Cu <sub>TG</sub> (%)	Beneficiation Units	Reagents	References
1	Cpy, cc, dg, bor, mal, cup, cv, qtz	Dexing copper Mine, China	0.443	23.16; 75.6	0.11	Classification and Flotation (3-stage)	SBX: PECTU as collector, Lime pH modifier	[71]
2	Cpy, cc, cv, py	Sungun Copper, Iran	0.61%	3.78; 87.03	0.09	Classification and Flotation	SIPX and AP407 as collector; Ether Polyglycol and MIBC as frother.	[153]
3	Cpy, py, po, asp, qtz	Mosabani copper mines, Singhbhum, India	1.5%	25; 96.86	0.05	Classification and Flotation (2-stage)	SIPX as collector, Pine oil as frother, soda ash as pH modifier	[156]
4	Cpy, cv, dg, py, mal, azu, qtz, kfs	Malanjkhand copper mines,	1.2%	25; 83.6	0.08	Classification and Flotation (3-stage)	SIPX as collector, Pine oil as frother, Lime as pH modifier	[156]



		Balaghat, India					
5	Cpy, sph, cv, bor	Cerro de Maimón copper mine, Dominican Republic	2.7	28; 83.3	0.49	Grinding, rougher flotation, regrinding, and cleaner flotation	Aero 9810 as collector, MIBC as frother, Lime as pH modifier [157]

cpy—chalcopyrite, cc—chalcocite, dg—digenite, bor—bornite, cv—covellite, mal—malachite, cup—cuprite, azu—azurite; po—pyrrhotite, asp—arsenopyrite, py—pyrite, qtz—quartz, kfs—k-feldspar, sph—sphalerite, Cu<sub>FG</sub>—feed copper grade, Cu<sub>CG</sub>—concentrate copper grade, Cu<sub>TG</sub>—tailing copper grade and Cu<sub>CR</sub>—recovery of copper.

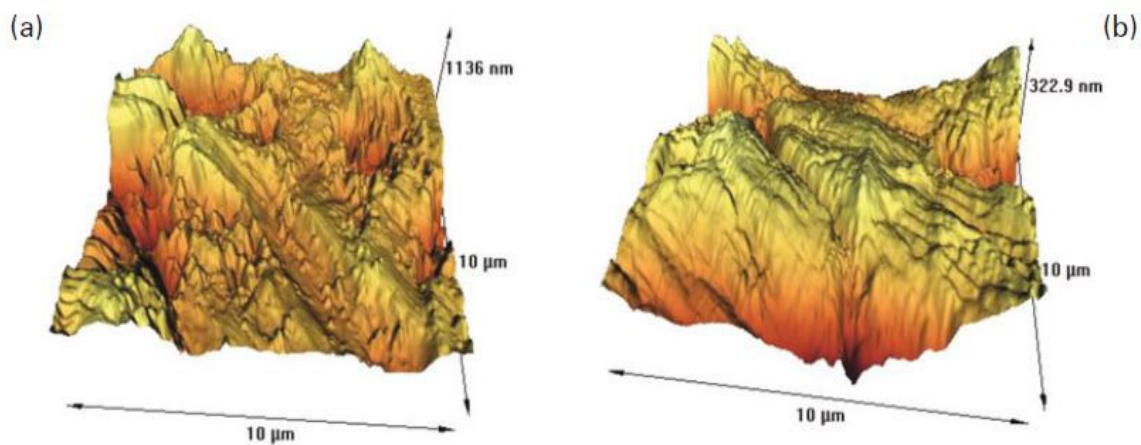
### 9. Future Prospect of Pretreatment Methods for Copper Minerals

From the point of view of copper's utilization in the future as a renewable and sustainable resource, we must adapt and develop an advanced process route to use all the low-grade copper deposits, tailing dams and overburden to meet the global supply-demand chain requirements.

#### 9.1. Microwave Pretreatment

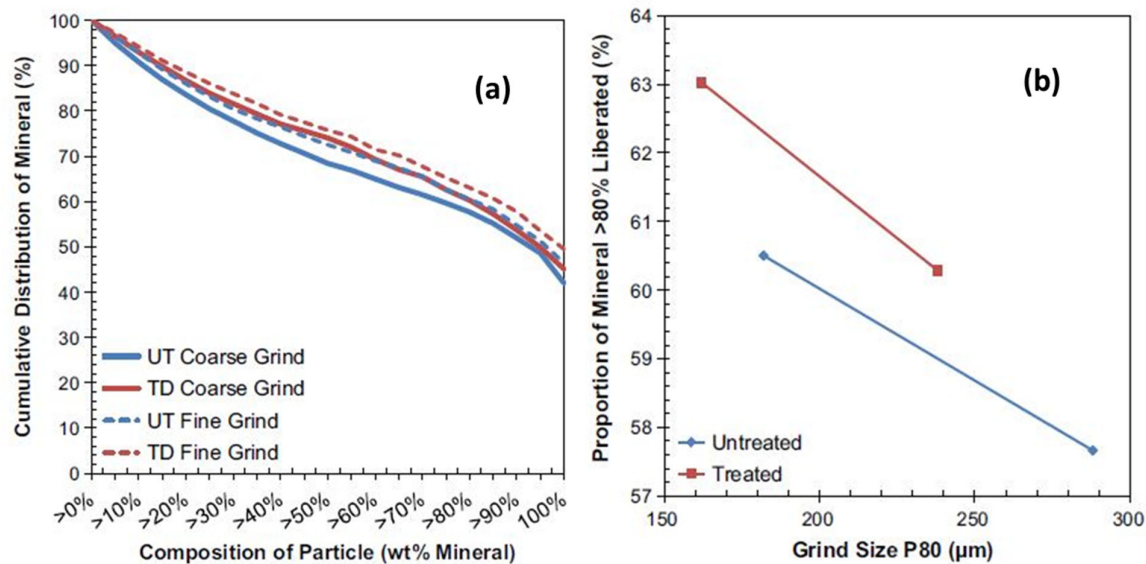
The microwave pretreatment method has been studied in the copper mineral to investigate its effect on the comminution characteristics [158–160]. The sieving breakage test outcome revealed a better efficiency of size reduction (increase up to 50%) for both porphyry and vein types of ores because of macro-fracture formations during the microwave treatment at their respective threshold temperatures. The bond grind ability of the porphyry type and vein type was increased up to 7% and 13%, respectively, at higher temperatures (i.e., above 400 °C) [158].

The effect of the microwave treatment on the chalcopyrite surface properties such as surface roughness and wettability has been studied [159]. It has been reported that the chalcopyrite surface's roughness reduces after exposure to microwave radiation (using AFM data), as shown in Figure 27. The iron oxide formation might ascribe it, along with surface oxidation. In comparison, the wettability of the chalcopyrite surface was increased with increasing the radiation period, which might be due to the reduced surface roughness [159].

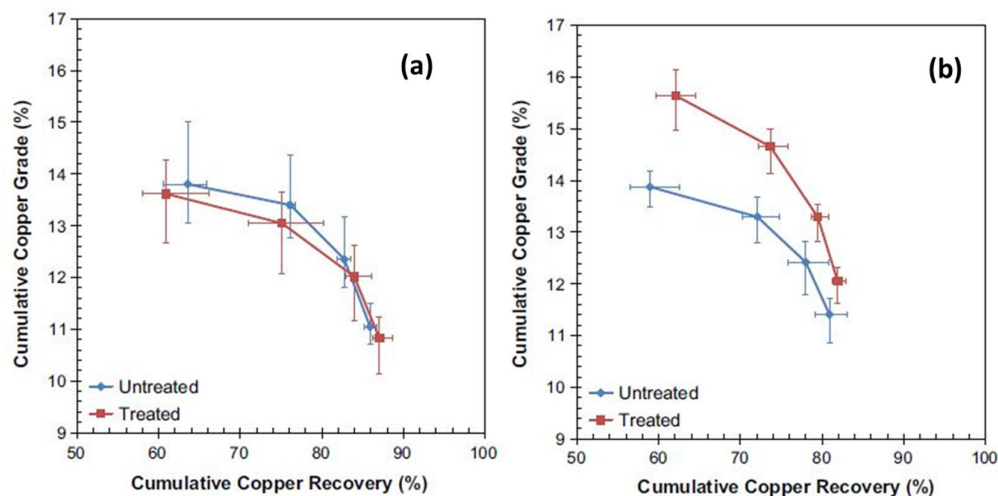


**Figure 27.** Three-dimensional AFM microphotograph images of a chalcopyrite surface (a) before and (b) after microwave radiation [159].

The impact of the microwave treatment on the liberation size and flotation operation for a copper sulphide ore has been also studied [160]. The results have confirmed that both treated coarser and finer particle materials have relatively higher degrees of liberation than untreated particles. It was observed that the microwave-treated coarse size particles ( $P_{80} = 238 \mu\text{m}$ ) produce around an equal percentage of liberation compared to the untreated finer-sized particles ( $P_{80} = 182 \mu\text{m}$ ) (Figure 28). Its selective breakage attributed to the increase in the percentage of liberation for copper sulphide at the grain boundaries. Due to the increasing liberation, the copper recovery through flotation slightly increased for the treated particles (Figure 29). The above literature concluded that microwave pre-treatment enhanced the grinding ability of the copper sulphide mineral (chalcopyrite rich) up to 50%, with a reduction in the surface roughness, which intensified the wettability of chalcopyrite and, hence, yielded a better flotation performance of the coarser size fraction at the laboratory/batch scale. However, their effect in large-scale flotation operations should be checked in the future with different types of copper sulphide minerals.



**Figure 28.** (a) Cumulative copper sulphide liberation by composition profiles, and (b) copper sulphide liberation versus grind size [160].



**Figure 29.** Copper-grade recovery curves for (a) fine-grained and (b) coarse grained materials under untreated and microwave-treated condition [160].

### 9.2. High-Voltage Pulse Treatment

The effect of a high-voltage pulse to improve the copper ore flotation has been recently studied [161,162]. This technique involves grain-induced preferential breakage under a controlled supply of pulse and size-wise separation of the feed material into body breakage and surface breakage products by ore grade splitting. It has been reported that, with increasing the voltage load, the copper grade increases due to the preferential breakage (Figure 30) [161]. More research should be carried out in this aspect for its applicability benefit in the mineral industry, especially in the comminution sector. More research should be carried out in this aspect for its applicability benefit in the mineral industry, especially in the comminution sector, which assist the methods of downstream process/beneficiation, i.e., size-based separation and breakage mode—multi-mineral separation. Research should be focused on liberation improvement, along with changes in the surface properties due to the pretreatment.

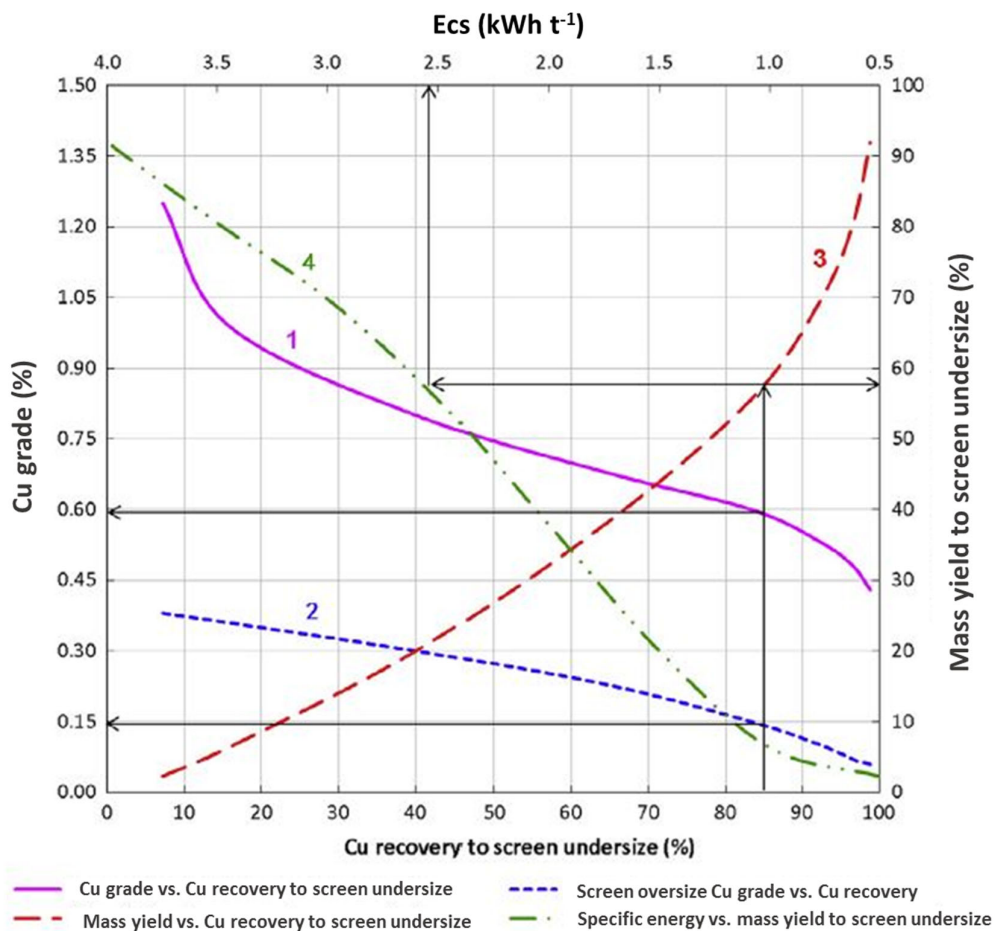
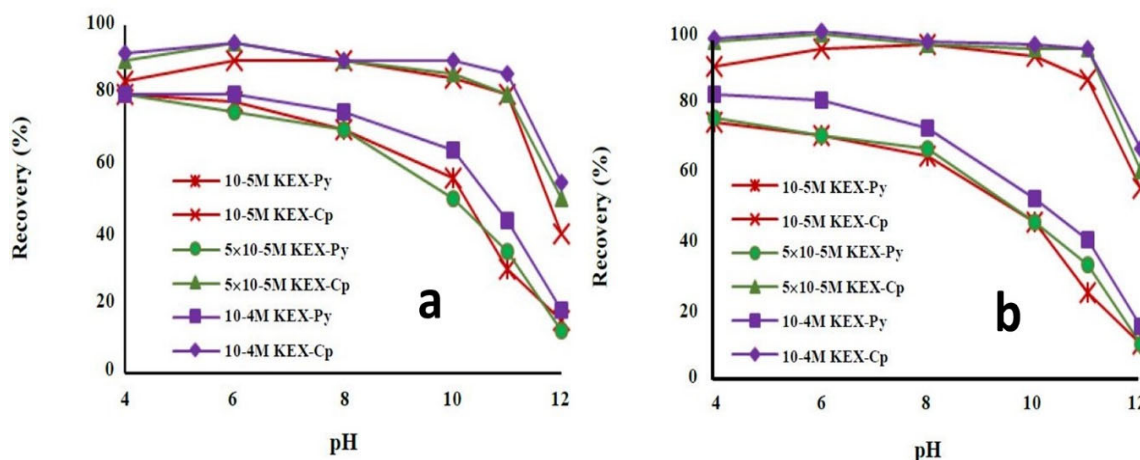


Figure 30. Proposed electrical pulse preconcentration characteristics curves [161].

### 9.3. Ultrasonic Pretreatment

Taheri and Lotfalian studied the effect of ultrasonic pretreatment on chalcopyrite flotation against pyrite [163]. The results of micro-flotation revealed that the selective flotation of chalcopyrite is possible by ultrasonic pretreatment and aeration. The ultrasonic pretreatment caused the desorption of precipitate metal hydroxide from the chalcopyrite surface and enhanced the chalcopyrite selective flotation from pyrite (Figure 31) [163]. The existing literature revealed that the selective separation of copper sulphide minerals

(mainly chalcopyrite) requires the selective depression of pyrite by flotation, which is difficult to achieve due to their (chalcopyrite and pyrite) galvanic interaction and involuntary activation of pyrite by the copper ion. However, the ultrasonic pretreatment method prior to flotation stated that the successful removal of metal hydroxide was possible from the chalcopyrite surface (caused by the galvanic interaction). It allowed the sulphide collector to adsorb preferentially on the chalcopyrite surface and resulted in enhanced chalcopyrite flotation as compared to pyrite. However, the effect of the ultrasonic pretreatment method may be applied in other copper sulphide minerals to compare its wider applicability.



**Figure 31.** Chalcopyrite (Cp) and pyrite (Py) recoveries as a function of the pH at different concentrations of KEX (a) before and (b) after ultrasonic treatment [163].

## 10. Summary

The current global economy demand for copper has been increased sharply because of its multiple applications in almost the whole sector, along with its never-ending reusability property throughout its life cycle assessment. From this review, it is clearly understood that copper flotation is the most extensively practiced beneficiation process. Primarily, the flotation of copper sulphide minerals was rigorously practiced using a thiol group collector, and the best results were achieved with xanthate. Due to the depletion of a high-grade sulphide deposit, many researchers' foci have shifted to the flotation of copper oxide minerals as a secondary resource. Traditional thiol collectors failed to float oxide copper in the concentrate. In comparison, the hydroxamate (chelating) group collector succeeded in copper oxide flotation. In the mixed ore (both copper sulphide and oxide), flotation was successfully performed using the concept of a mixed collector, i.e., mixing thiol and hydroxamate in a definite proportion. A bio-collector, i.e., canola oil, was also used for the selective flotation of chalcopyrite against pyrite.

Apart from physicochemical separation, the gravity concentration technique was also adopted, only if a significant difference in their specific gravity was observed between copper and the gangue mineral. Most of the time, gravity separation is used as a pre-concentration step before the flotation process. In the case of ultrafine particles, flotation became inefficient, and hence, many researchers have tried the flocculation of copper minerals using classical flocculants and bioflocculent. Due to its smaller capacity, its applicability has been limited to the dewatering unit. Copper tailing is also considered a potential source of copper. Many researchers have successfully recovered copper from processed tailings, for example, by using a Knelson separator. Advanced pretreatment technologies such as microwave pretreatment, high-voltage pulse treatment and ultrasonic pretreatment were also investigated for processing copper ore to ease the downstream process. The copper minerals subjected to microwave treatment resulted in a better efficiency during the comminution process, which may be due to the formation of macro-fractures, and

resulted in a higher degree of liberation, along with a decrease in the mineral surface roughness. Similarly, the high-voltage pulse treatment was practiced on rejected copper lumps for preferential breakage. The ultrasonic treatment enhanced the selective flotation recovery of chalcopyrite against pyrite due to the desorption of metal hydroxide precipitate from its surface. The visualization analysis showed the recent trends followed for copper ore processing and found that flotation is the leading research area.

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## References

1. LePan, N. Visualizing Copper's Role in the Transition to Clean Energy. Available online: <https://www.visualcapitalist.com/visualizing-coppers-role-in-the-transition-to-clean-energy/> (accessed on 6 March 2022).
2. Moreno-Leiva, S.; Haas, J.; Junne, T.; Valencia, F.; Godin, H.; Kracht, W.; Nowak, W.; Eltrop, L. Renewable energy in copper production: A review on systems design and methodological approaches. *J. Clean. Prod.* **2020**, *246*, 118978. <https://doi.org/10.1016/j.jclepro.2019.118978>.
3. Hund, K.; La Porta, D.; Fabregas, T.; Laing, T.; Drexhage, J. *Minerals for Climate Action: The Mineral Intensity of the Clean Energy Transition*; World Bank Group; World Bank: Washington, DC, USA, 2020.
4. International Copper Association and the Copper Alliance®—Copper Alliance. Available online: <https://copperalliance.org/> (accessed on 3 September 2020).
5. Copper Development Association Inc. *Copper's Bright Past and Brighter Future*; Copper Development Association Inc.: New York, NY, USA, 2022.
6. Bide, T. *British Geological Survey Report—Copper*; NERC Open Research Archive: Nottingham, UK, 2007.
7. Schipper, B.W.; Lin, H.-C.; Meloni, M.A.; Wansleben, K.; Heijungs, R.; van der Voet, E. Estimating global copper demand until 2100 with regression and stock dynamics. *Resour. Conserv. Recycl.* **2018**, *132*, 28–36. <https://doi.org/10.1016/j.resconrec.2018.01.004>.
8. Prasad, U. *Economic Geology: Economic Mineral Deposits*; CBS Pub.: New Delhi, India, 2006; ISBN 812-390-460-6.
9. Kleijn, R.; van der Voet, E.; Kramer, G.J.; van Oers, L.; van der Giesen, C. Metal requirements of low-carbon power generation. *Energy* **2011**, *36*, 5640–5648. <https://doi.org/10.1016/j.energy.2011.07.003>.
10. Evans, A.M. *Ore Geology and Industrial Minerals: An Introduction*; John Wiley & Sons: Hoboken, NJ, USA, 2009; ISBN 144-431-405-X.
11. Skinner, B.J. Chapter 10 A Second Iron Age Ahead? In *Studies in Environmental Science*; Elsevier: Amsterdam, The Netherlands, 1979; Volume 3, pp. 559–575. [https://doi.org/10.1016/s0166-1116\(08\)71071-9](https://doi.org/10.1016/s0166-1116(08)71071-9).
12. Guy, P.; Trahar, W. *The Effects of Oxidation and Mineral Interaction on Sulphide Flotation*; Elsevier: Amsterdam, The Netherlands, 1985.
13. Trahar, W. A rational interpretation of the role of particle size in flotation. *Int. J. Miner. Process.* **1981**, *8*, 289–327. [https://doi.org/10.1016/0301-7516\(81\)90019-3](https://doi.org/10.1016/0301-7516(81)90019-3).
14. Zhang, X.; Han, Y.; Kawatra, S.K. Effects of Grinding Media on Grinding Products and Flotation Performance of Sulfide Ores. *Miner. Process. Extr. Met. Rev.* **2021**, *42*, 172–183. <https://doi.org/10.1080/08827508.2019.1692831>.
15. Molaei, N.; Hoseinian, F.S.; Rezai, B. A Study on the Effect of Active Pyrite on Flotation of Porphyry Copper Ores. *Physicochem. Probl. Miner. Process.* **2018**, *54*, 922–933.
16. Jena, S.; Pattanaik, A.; Venugopal, R. Statistical Analysis of Species Interaction and Optimization of Copper Flotation Process. *J. Mines Met. Fuels* **2019**, *67*, 326–331.
17. Abramov, A.A.; Forssberg, K.S.E. Chemistry and Optimal Conditions for Copper Minerals Flotation: Theory and Practice. *Miner. Process. Extr. Met. Rev.* **2005**, *26*, 77–143. <https://doi.org/10.1080/08827500590883197>.
18. Bakalarz, A.; Gloy, G.; Luszczkiewicz, A. Flotation of Sulfide Components of Copper Ore in the Presence of n-Dodecane. *Miner. Process. Extr. Met. Rev.* **2015**, *36*, 103–111. <https://doi.org/10.1080/08827508.2014.898301>.
19. Gül, A. The Role of Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and Activated Carbon on the Selective Flotation of Chalcopyrite from a Copper Ore Using a Dithiophosphine-Type Collector. *Miner. Process. Extr. Met. Rev.* **2007**, *28*, 235–245. <https://doi.org/10.1080/08827500601141750>.



20. Katwika, C.N.; Kime, M.-B.; Kalenga, P.N.M.; Mbuya, B.I.; Mwilen, T.R. Application of Knelson Concentrator for Beneficiation of Copper–Cobalt Ore Tailings. *Miner. Process. Extr. Met. Rev.* **2019**, *40*, 35–45. <https://doi.org/10.1080/08827508.2018.1481057>.
21. Poulter, S.; Fitzmaurice, C.; Steward, G. The Knelson Concentrator: Application and Operation at Rosebery. In Proceedings of the 5th Mill Operators Conf, Roxby Downs, Australia, 16–20 October 1994.
22. Ramakokovhu, M.M.; Kasaini, H.; Mbaya, R.K. Leaching Characteristics of Upgraded Copper Flotation Tailings. *Int. J. Mater. Metall. Eng.* **2012**, *6*, 859–863.
23. Kime, M.B.; Kaniki, A.T. Determining milling parameters of a pear-shaped ball mill for grinding high-talc oxidized copper-cobalt ore. *Econ. Anal.* **2017**, *8*, 136306708.
24. Perek, K.T.; Arslan, F. Effect of Mechanical Activation on Pressure Leaching of Küre Massive Rich Copper Ore. *Miner. Process. Extr. Met. Rev.* **2010**, *31*, 191–200. <https://doi.org/10.1080/08827508.2010.483358>.
25. Mweene, L.; Subramanian, S. Selective Dispersion-Flocculation and Flotation Studies on a Siliceous Copper Ore. *Physicochem. Probl. Miner. Process.* **2018**, *54*, 1282–1291.
26. Patra, P.; Natarajan, K. Microbially induced flocculation and flotation for separation of chalcopyrite from quartz and calcite. *Int. J. Miner. Process.* **2004**, *74*, 143–155. <https://doi.org/10.1016/j.minpro.2003.10.006>.
27. Acar, S.; Somasundaran, P. Flocculation of sulfides and the role of a complexing agent in it. *Int. J. Miner. Process.* **1989**, *27*, 111–123. [https://doi.org/10.1016/0301-7516\(89\)90009-4](https://doi.org/10.1016/0301-7516(89)90009-4).
28. Copper Reserves by Country. 2020. Available online: <https://www.statista.com/statistics/273637/copper-reserves-by-country/> (accessed on 7 March 2022).
29. Dong, D.; van Oers, L.; Tukker, A.; van der Voet, E. Assessing the Future Environmental Impacts of Copper Production in China: Implications of the Energy Transition. *J. Clean. Prod.* **2020**, *274*, 122825.
30. International Copper Study Group. *The World Copper Factbook*; International Copper Study Group: Lisbon, Portugal, 2014.
31. U.S. Geological Survey. *Mineral Commodity Summaries 2020*; U.S. Geological Survey: Reston, VA, USA, 2020; p. 204.
32. Banger, K.M. Principles of Engineering Geology. Available online: <https://firstwaybookshop.com/product/textbook-of-geology-general-and-engineering-by-k-m-bangar/> (accessed on 7 March 2022).
33. Sillitoe, R. *Copper Provinces*. Society of Economic Geologists; Special Publication, London, UK, 2012; Volume 16, pp. 1–18.
34. Tatsch, J.H. *Copper Deposits: Origin, Evolution, and Present Characteristics: An Analysis of the Present Copper Deposits in Terms of the Geometrical, Mechanical, Thermal, and Chemical Aspects of the Earth's Behavior during the Past 4.6 Billion Years*; Tatsch Associates: Coos Bay, OR, USA, 1975; ISBN 0-912890-08-8.
35. Bateman, A. *Economic Mineral Deposits*; John Wiley & Sons, Inc.: Carrollton, TX, USA, 1975.
36. Wills, B.; Napier-Munn, T.; Julius Kruttschnitt Mineral Research Centre. *Wills' Mineral Processing Technology: An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery*; Butterworth-Heinemann: Oxford, UK, 2006.
37. Fuerstenau, M.; Jameson, G.; Yoon, R. *Froth Flotation: A Century of Innovation*; Society for Mining, Metallurgy, and Exploration Inc.: Littleton, CO, USA, 2007; 8975p.
38. Ancia, P. Comparison of the Knelson and Falcon Centrifugal Separators, Proceedings of the Proc. Conf. on Innovation in Physical Separation Technologies, Richard Mozley Symp., Falmouth, UK, 4–5 June 1997; Mozeley, R., Ed.; University of Liège: Liège, Belgium, 1997; pp. 53–62.
39. Jena, S.S.; Angadi, S.I.; Mandre, N.R.; Venugopal, R. An Investigation into Pre-concentration of Low-Grade Silica-Rich Malanjkhand Copper Ore by Wilfley Table. *Trans. Indian Inst. Met.* **2021**, *74*, 571–581. <https://doi.org/10.1007/s12666-020-02160-y>.
40. Carta, M.; Ghiani, M.; Rossi, G. Beneficiation of a Complex Sulfide Ore by an Integrated Process of Flotation and Bioleaching. *Complex Sulphide Ores* **1980**, 178–185.
41. Chadwick, J. CAMEC-The Cobalt Champion, Reports on What Is Today Probably the Leading Cobalt Miner in the World. *Int. Min.* **2008**, 8–16.
42. Lutandula, M.S.; Maloba, B. Recovery of cobalt and copper through reprocessing of tailings from flotation of oxidised ores. *J. Environ. Chem. Eng.* **2013**, *1*, 1085–1090. <https://doi.org/10.1016/j.jece.2013.08.025>.
43. Jena, S.S.; Gharai, M.; Mandre, N.R.; Venugopal, R. Mineralogical Characterization and Gravity Separation of Lean Grade Mixed Copper Ore of Malanjkhand Deposit. *Trans. Indian Inst. Met.* **2019**, *72*, 245–255. <https://doi.org/10.1007/s12666-018-1478-6>.
44. Yarar, B.; Kitchener, J. Selective Flocculation of Minerals. Pt. 1. Basic Principles. Pt. 2. Experimental Investigation of Quartz, Calcite, and Galena. *Trans. Inst. Min. Met.* **1970**, *79*, 760.
45. Sresty, G.; Somasundaran, P. Selective flocculation of synthetic mineral mixtures using modified polymers. *Int. J. Miner. Process.* **1980**, *6*, 303–320. [https://doi.org/10.1016/0301-7516\(80\)90027-7](https://doi.org/10.1016/0301-7516(80)90027-7).
46. Ackerman, P.; Harris, G.; Klimpel, R.; Aplan, F. Evaluation of flotation collectors for copper sulfides and pyrite, I. Common sulfhydryl collectors. *Int. J. Miner. Process.* **1987**, *21*, 105–127. [https://doi.org/10.1016/0301-7516\(87\)90009-3](https://doi.org/10.1016/0301-7516(87)90009-3).
47. Attia, Y.; Kitchener, J. Development of Complexing Polymers for the Selective Flocculation of Copper Minerals. In Proceedings of 11th International Mineral Processing Congress, Cagliari, Italy, 20–26 April 1975.
48. Heyes, G.; Trahar, W. The Natural Flotability of Chalcopyrite. *Int. J. Miner. Process.* **1977**, *4*, 317–344.
49. Yoon, R. Collectorless flotation of chalcopyrite and sphalerite ores by using sodium sulfide. *Int. J. Miner. Process.* **1981**, *8*, 31–48. [https://doi.org/10.1016/0301-7516\(81\)90005-3](https://doi.org/10.1016/0301-7516(81)90005-3).
50. Luttrell, G.H.; Yoon, R.-H. The collectorless flotation of chalcopyrite ores using sodium sulfide. *Int. J. Miner. Process.* **1984**, *13*, 271–283. [https://doi.org/10.1016/0301-7516\(84\)90048-6](https://doi.org/10.1016/0301-7516(84)90048-6).

51. Mitchell, T.K.; Nguyen, A.; Evans, G.M. Heterocoagulation of chalcopyrite and pyrite minerals in flotation separation. *Adv. Colloid Interface Sci.* **2005**, *114*, 227–237. <https://doi.org/10.1016/j.cis.2004.08.009>.
52. Gardner, J.; Woods, R. An electrochemical investigation of the natural flotability of chalcopyrite. *Int. J. Miner. Process.* **1979**, *6*, 1–16. [https://doi.org/10.1016/0301-7516\(79\)90028-0](https://doi.org/10.1016/0301-7516(79)90028-0).
53. Trahar, W. A laboratory study of the influence of sodium sulphide and oxygen on the collectorless flotation of chalcopyrite. *Int. J. Miner. Process.* **1983**, *11*, 57–74. [https://doi.org/10.1016/0301-7516\(83\)90044-3](https://doi.org/10.1016/0301-7516(83)90044-3).
54. Allison, S.A.; Goold, L.A.; Nicol, M.; Granville, A. A determination of the products of reaction between various sulfide minerals and aqueous xanthate solution, and a correlation of the products with electrode rest potentials. *Metall. Trans.* **1972**, *3*, 2613–2618. <https://doi.org/10.1007/bf02644237>.
55. Leppinen, J.; Basilio, C.; Yoon, R. In-situ FTIR study of ethyl xanthate adsorption on sulfide minerals under conditions of controlled potential. *Int. J. Miner. Process.* **1989**, *26*, 259–274. [https://doi.org/10.1016/0301-7516\(89\)90032-x](https://doi.org/10.1016/0301-7516(89)90032-x).
56. Venugopal, R.; Viswanatha, D.; Sanyal, P.; Rao, T.C. Flotation Characteristics of Chalcopyrite Ore. *Inst. Eng. J.-MN* **1993**, *74*, 12–16.
57. Ram, A.; Venugopal, R.; Rao, T. Reagent-Particle Size Interaction in Copper Ore Flotation. *Trans. Indian Inst. Met.* **1990**, *43*, 356–362.
58. Dhar, P.; Thornhill, M.; Kota, H.R. Comparison of single and mixed reagent systems for flotation of copper sulphides from Nussir ore. *Miner. Eng.* **2019**, *142*, 105930. <https://doi.org/10.1016/j.mineng.2019.105930>.
59. Dhar, P.; Thornhill, M.; Kota, H.R. Investigation of Copper Recovery from a New Copper Ore Deposit (Nussir) in Northern Norway: Dithiophosphates and Xanthate-Dithiophosphate Blend as Collectors. *Minerals* **2019**, *9*, 146. <https://doi.org/10.3390/min9030146>.
60. Dhar, P.; Thornhill, M.; Kota, H.R. Investigation of Copper Recovery from a New Copper Deposit (Nussir) in Northern Norway. *Miner. Process. Extr. Met. Rev.* **2019**, *40*, 380–389. <https://doi.org/10.1080/08827508.2019.1635475>.
61. Owusu, C.; Fornasiero, D.; Addai-Mensah, J.; Zanin, M. Influence of pulp aeration on the flotation of chalcopyrite with xanthate in chalcopyrite/pyrite mixtures. *Int. J. Miner. Process.* **2015**, *134*, 50–57. <https://doi.org/10.1016/j.minpro.2014.10.013>.
62. Hangone, G.; Bradshaw, D.; Ekmekci, Z. Flotation of a Copper Sulphide Ore from Okiep Using Thiol Collectors and Their Mixtures. *J. South. Afr. Inst. Min. Metall.* **2005**, *105*, 199–206.
63. Finkelstein, N.; Poling, G. *The Role of Dithiolates in the Flotation of Sulphide Minerals*; Mintek: Randburg, South Africa, 1977.
64. Fuerstenau, M. Thiol Collector Adsorption Processes. *US Bur. Mines Inf. Circ.* **1980**, *8818*, 7–23.
65. Harris, P.; Finkelstein, N. The Interaction of Chalcocite, Oxygen and Xanthates, National Institute for Metallurgy, Randburg, South Africa. Report No. 1895. *Int. J. Mineral Processing* **1977**, *12*, 33–37.
66. Fuerstenau, M. Chemistry of Collectors in Solution. South African Institute of Mining and Metallurgy. In *Principles of Flotation*; SAIMM: Johannesburg, South Africa, 1982; pp. 1–16.
67. Sheridan, M.; Nagaraj, D.; Fornasiero, D.; Ralston, J. The use of a factorial experimental design to study collector properties of N-allyl-O-alkyl thionocarbamate collector in the flotation of a copper ore. *Miner. Eng.* **2002**, *15*, 333–340. [https://doi.org/10.1016/S0892-6875\(02\)00037-7](https://doi.org/10.1016/S0892-6875(02)00037-7).
68. Wang, D. *Flotation Reagents: Applied Surface Chemistry on Minerals Flotation and Energy Resources Beneficiation*; Springer: Berlin/Heidelberg, Germany, 2016; ISBN 981-102-028-0.
69. Hanson, J.S.; Fuerstenau, D.W. The electrochemical and flotation behavior of chalcocite and mixed oxide/sulfide ores. *Int. J. Miner. Process.* **1991**, *33*, 33–47. [https://doi.org/10.1016/0301-7516\(91\)90041-g](https://doi.org/10.1016/0301-7516(91)90041-g).
70. Twidle, T.R.; Engelbrecht, P.C. Developments in the Flotation of Copper at Black Mountain. *J. South. Afr. Inst. Min. Metall.* **1984**, *84*, 164–178.
71. Liu, G.; Zhong, H.; Xia, L.; Wang, S.; Xu, Z. Improving copper flotation recovery from a refractory copper porphyry ore by using ethoxycarbonyl thiourea as a collector. *Miner. Eng.* **2011**, *24*, 817–824. <https://doi.org/10.1016/j.mineng.2011.01.009>.
72. Xiong, K.; Zheng, G.S. *Process Mineralogy and Flotation Kinetic of a Copper Oxide Ore during Sulfuration Flotation*; Trans Tech Publication: Freienbach, Switzerland, 2013; Volume 634, pp. 3460–3465.
73. Farrokhpay, S.; Ametov, I.; Grano, S. Improving the recovery of low grade coarse composite particles in porphyry copper ores. *Adv. Powder Technol.* **2011**, *22*, 464–470. <https://doi.org/10.1016/j.apt.2011.04.003>.
74. Farrokhpay, S. Effect of Feed Classification by Hydrocycloning on Copper Recovery in Flotation. *Can. Metall. Quart.* **2010**, *49*, 107–112.
75. Chander, S.; Fuerstenau, D. The Effect of Potassium Diethyldithiophosphate on the Electrochemical Properties of Platinum, Copper and Copper Sulfide in Aqueous Solutions. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *56*, 217–247.
76. Schlesinger, M.E.; Sole, K.C.; Davenport, W.G.; Alvear, G.R. *Extractive Metallurgy of Copper*; Elsevier: Amsterdam, The Netherlands, 2021; ISBN 012-821-903-3.
77. Ge, B.L.; Fu, Y.X.; Li, Q. *A Copper Oxide Ore Treatment by Flotation*; Trans Tech Publication: Freienbach, Switzerland, 2013; Volume 813, pp. 230–233.
78. Bulatovic, S. Flotation of Oxide Copper and Copper Cobalt Ores. In *Handbook of Flotation Reagents: Chemistry, Theory and Practice*; Elsevier: Amsterdam, The Netherlands, 2010; Volume 2, pp. 47–65.
79. Herrera-Urbina, R.; Laskowski, J.; Fuerstenau, D. A Process for the Flotation of Chrysocolla. In Proceedings of the In XXV International Mineral Processing Congress Proceeding, Brisbane, Australia, 6–10 September 2010; pp. 1959–1969.



80. Lee, K.; Archibald, D.; McLean, J.; Reuter, M.A. Flotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectors. *Miner. Eng.* **2009**, *22*, 395–401. <https://doi.org/10.1016/j.mineng.2008.11.005>.
81. Lenormand, J.; Salman, T.; Yoon, R. Hydroxamate Flotation of Malachite. *Can. Metall. Q.* **1979**, *18*, 125–129.
82. Ziyadanogullari, R.; Aydin, F. A New Application for Flotation of Oxidized Copper Ore. *J. Miner. Mater. Charact. Eng.* **2005**, *4*, 67–73.
83. Glembotskii, V.; Klassen, V.; Plaksin, I. *Flotation; Primary Sources*: New York, NY, USA, 1972.
84. Marion, C.; Jordens, A.; Li, R.; Rudolph, M.; Waters, K. An evaluation of hydroxamate collectors for malachite flotation. *Sep. Purif. Technol.* **2017**, *183*, 258–269. <https://doi.org/10.1016/j.seppur.2017.02.056>.
85. Choi, J.; Choi, S.Q.; Park, K.; Han, Y.; Kim, H. Flotation behaviour of malachite in mono- and di-valent salt solutions using sodium oleate as a collector. *Int. J. Miner. Process.* **2016**, *146*, 38–45. <https://doi.org/10.1016/j.minpro.2015.11.011>.
86. Li, F.; Zhong, H.; Xu, H.; Jia, H.; Liu, G. Flotation behavior and adsorption mechanism of  $\alpha$ -hydroxyoctyl phosphinic acid to malachite. *Miner. Eng.* **2015**, *71*, 188–193. <https://doi.org/10.1016/j.mineng.2014.11.013>.
87. Peterson, H.; Fuerstenau, M.; Rickard, R.; Miller, J. Chrysocolla Flotation by the Formation of Insoluble Surface Chelates. *Trans. Am. Inst. Min. Eng.* **1965**, *232*, 388–392.
88. Yang, X.F.; Liu, Q.J.; Deng, R.D. *Flotation of Copper Oxide Minerals Using Ethylene Phosphate as Activators*; Trans Tech Publication: Freienbach, Switzerland, 2012; Volume 581, pp. 975–982.
89. Lee, J.; Nagaraj, D.; Coe, J. Practical aspects of oxide copper recovery with alkyl hydroxamates. *Miner. Eng.* **1998**, *11*, 929–939. [https://doi.org/10.1016/S0892-6875\(98\)00080-6](https://doi.org/10.1016/S0892-6875(98)00080-6).
90. Feng, Q.; Zhao, W.; Wen, S.; Cao, Q. Copper sulfide species formed on malachite surfaces in relation to flotation. *J. Ind. Eng. Chem.* **2017**, *48*, 125–132. <https://doi.org/10.1016/j.jiec.2016.12.029>.
91. Zhu, R.; Gu, G.; Chen, Z.; Wang, Y.; Song, S. A New Collector for Effectively Increasing Recovery in Copper Oxide Ore-Staged Flotation. *Minerals* **2019**, *9*, 595. <https://doi.org/10.3390/min9100595>.
92. Rao, S.; Finch, J. Base metal oxide flotation using long chain xanthates. *Int. J. Miner. Process.* **2002**, *69*, 251–258. [https://doi.org/10.1016/S0301-7516\(02\)00130-8](https://doi.org/10.1016/S0301-7516(02)00130-8).
93. Li, Z.; Rao, F.; Lou, X.; Song, S.; López-Valdivieso, A. Floc-Flotation of Malachite Fines with an Octyl Hydroxamate and Kerosene Mixture. *Minerals* **2019**, *9*, 301. <https://doi.org/10.3390/min9050301>.
94. Sun, Q.-Y.; Yin, W.-Z.; Li, D.; Fu, Y.-F.; Xue, J.-W.; Yao, J. Improving the sulfidation–flotation of fine cuprite by hydrophobic flocculation pretreatment. *Int. J. Miner. Met. Mater.* **2018**, *25*, 1256–1262. <https://doi.org/10.1007/s12613-018-1678-4>.
95. Liu, J.; Hu, Z.; Liu, G.; Huang, Y.; Zhang, Z. Selective Flotation of Copper Oxide Minerals with A Novel Amino-Triazole-Thione Surfactant: A Comparison to Hydroxamic Acid Collector. *Miner. Process. Extr. Met. Rev.* **2019**, *41*, 96–106. <https://doi.org/10.1080/08827508.2019.1575214>.
96. Fuerstenau, D.; Herrera-Urbina, R.; Laskowski, J. Surface Properties and Flotation Behaviour of Chrysocolla in the Presence of Potassium Octylhydroxamate. In Proceedings of the 2nd Latin-American Congr. Froth Flotation, Concepcion, Chile, 19–23 August 1985; pp. 19–23.
97. Liu, J.; Liu, G.; Huang, Y.; Zhang, Z. Tetrazinan-thione collectors for copper oxide mineral: Synthesis and flotation mechanism. *Appl. Surf. Sci.* **2019**, *491*, 624–632. <https://doi.org/10.1016/j.apsusc.2019.06.196>.
98. Aplan, F.; Fuerstenau, D. The Flotation of Chrysocolla by Mercaptan. *Int. J. Miner. Process.* **1984**, *13*, 105–115.
99. Barbaro, M.; Urbina, R.H.; Cozza, C.; Fuerstenau, D.; Marabini, A. Flotation of oxidized minerals of copper using a new synthetic chelating reagent as collector. *Int. J. Miner. Process.* **1997**, *50*, 275–287. [https://doi.org/10.1016/S0301-7516\(97\)00045-8](https://doi.org/10.1016/S0301-7516(97)00045-8).
100. Nagaraj, D.; Somasundaran, P. Commercial Chelating Extractants as Collectors: Flotation of Copper Minerals Using “LIX” Reagents. *Trans. Am. Inst. Min. Engrs.* **1979**, *266*, 1892–1897.
101. Xiong, K.; Wen, S.M.; Zheng, G.S.; Bai, S.J.; Shen, H.Y. *Flotation Research on Cuprite-Type Oxide Copper in XinJiang*; Trans Tech Publication: Freienbach, Switzerland, 2012; Volume 524, pp. 987–992.
102. Han, G.; Wen, S.; Wang, H.; Feng, Q. Surface sulfidization mechanism of cuprite and its response to xanthate adsorption and flotation performance. *Miner. Eng.* **2021**, *169*, 106982. <https://doi.org/10.1016/j.mineng.2021.106982>.
103. Han, G.; Wen, S.; Wang, H.; Feng, Q. Sulfidization regulation of cuprite by pre-oxidation using sodium hypochlorite as an oxidant. *Int. J. Min. Sci. Technol.* **2021**, *31*, 1117–1128. <https://doi.org/10.1016/j.ijmst.2021.11.001>.
104. Rule, W.T. Recovery of Copper from Copper Oxide Minerals. **1982**.
105. Wang, Y.J.; Wen, S.M.; Liu, D.; Cao, Q.B.; Feng, Q.C.; Lv, C. *Sulphidizing Flotation of Copper Oxide Ore*; Trans Tech Publication: Freienbach, Switzerland, 2013; Volume 807, pp. 2279–2283.
106. Zhao, Y.; Liu, S.; Liu, H.; Wang, D.; Li, T. *Flotation Test of a High Silica Copper Oxide Ore in Yunnan*; Atlantis Press: Paris, France, 2015.
107. Saleh, A.-H.M.; Ramadan, A.M.; Moharam, M.R. Beneficiation of Egyptian Abu-Swayel Copper Ore by Flotation. *Physicochem. Probl. Miner. Process.* **2008**, *42*, 119–130.
108. Singh, R.; Chandrashekhar, S.; Rath, R.; Nayak, B.; Bhattacharyya, K. Designing Process for Concentration of a Low Grade Copper Ore. In Proceedings of the International Seminar on Mineral Processing Technology, Trivandrum, India, 22–24 April 2008; pp. 1–6.
109. Arakatsu, A.; Nakazawa, H.; Naruse, H. Rotating multitube biocontactor for treating sewage. Patent No. 4,022,689, 1977.
110. Pang, W.H.; Liu, Q.J.; Ding, P. *Experimental Research on Flotation of Copper Oxide Ore in Guizhou*; Trans Tech Publication: Freienbach, Switzerland, 2013; Volume 813, pp. 238–241.

111. Ou, L.M.; Yin, B.Y. *A Flotation Technique for a Sulfide-Oxidized Cu-Co Mixed Ore*; Trans Tech Publication: Freienbach, Switzerland, 2012; Volume 402, pp. 564–571.
112. Xiong, F.; Li, Y.J.; Zhang, Z.H.; Lan, Y.Z. *Flotation Response of the Refractory Yangla Copper Oxide Ores with Hydroxamate Collectors*; Trans Tech Publication: Freienbach, Switzerland, 2013; Volume 803, pp. 131–136.
113. Xiong, F.; Li, Y.J.; Zhang, Z.; Du, G.F.; Lan, Y.Z. *Application of Chelating Collectors in the Flotation of Copper Minerals*; Trans Tech Publication: Freienbach, Switzerland, 2013; Volume 868, pp. 417–422.
114. Cao, Z.-F.; Zhong, H.; Liu, G.-Y.; Zhao, S.-J. Techniques of copper recovery from Mexican copper oxide ore. *Min. Sci. Technol.* **2009**, *19*, 45–48. [https://doi.org/10.1016/S1674-5264\(09\)60009-0](https://doi.org/10.1016/S1674-5264(09)60009-0).
115. Prabhakar, S.; Bhaskar Raju, G.; Misra, V.; Khangaonkar, P. Studies on the Flotation of Mixed Oxide-Sulphide Ores of Copper from Malankhand Deposit India. In *Minerals, Materials and Industry, Proceedings of the 14th Congress of the Council of Mining and Metallurgy Institutions, Edinburgh, Scotland, 2–6 July 1990*; The Institution of Mining and Metallurgy: London, UK, 1990.
116. Phetla, T.P.; Muzenda, E. A Multistage Sulphidisation Flotation Procedure for a Low Grade Malachite Copper Ore. *Int. J. Chem. Nucl. Mater. Metall. Eng.* **2010**, *4*, 26–32.
117. Subramanian, S.; Natarajan, K. Zeta Potential Studies on Some Iron Ore Minerals in the Presence of Starches. *Trans. Indian Inst. Met.* **1988**, *41*, 255–263.
118. Quast, K. A review of hematite flotation using 12-carbon chain collectors. *Miner. Eng.* **2000**, *13*, 1361–1376. [https://doi.org/10.1016/S0892-6875\(00\)00119-9](https://doi.org/10.1016/S0892-6875(00)00119-9).
119. Kallay, N.; Torbić, Z.; Barouch, E.; Jednačak-Bišćan, J. The determination of isoelectric point for metallic surfaces. *J. Colloid Interface Sci.* **1987**, *118*, 431–435. [https://doi.org/10.1016/0021-9797\(87\)90479-6](https://doi.org/10.1016/0021-9797(87)90479-6).
120. Salopek, B.; Krasic, D.; Filipovic, S. Measurement and Application of Zeta-Potential. *Rud.-Geol.-Naft. Zb.* **1992**, *4*, 147.
121. Ottewill, R.H. The Rideal Lecture. Colloidal Dispersions. *Faraday Discuss. Chem. Soc.* **1990**, *90*, 1–15.
122. Mokone, T.; van Hille, R.; Lewis, A. Effect of solution chemistry on particle characteristics during metal sulfide precipitation. *J. Colloid Interface Sci.* **2010**, *351*, 10–18. <https://doi.org/10.1016/j.jcis.2010.06.027>.
123. Kosmulski, M. *Surface Charging and Points of Zero Charge*; CRC Press: Boca Raton, FL, USA, 2009; ISBN 042-909-339-X.
124. Reyes-Bozo, L.; Escudey, M.; Vyhmeister, E.; Higuera, P.; Godoy-Faúndez, A.; Salazar, J.L.; Valdés-González, H.; Wolf-Sepúlveda, G.; Herrera-Urbina, R. Adsorption of biosolids and their main components on chalcopirite, molybdenite and pyrite: Zeta potential and FTIR spectroscopy studies. *Miner. Eng.* **2015**, *78*, 128–135. <https://doi.org/10.1016/j.mineng.2015.04.021>.
125. Rath, R.; Subramanian, S.; Sivanandam, V.; Pradeep, T. Studies on the Interaction of Guar Gum with Chalcopirite. *Can. Metall. Q.* **2001**, *40*, 1–11.
126. Júnior, J.A.A.; Baldo, J.B. The Behavior of Zeta Potential of Silica Suspensions. *New J. Glass Ceram.* **2014**, *4*, 29–37. <https://doi.org/10.4236/njgc.2014.42004>.
127. Fullston, D.; Fornasiero, D.; Ralston, J. Zeta Potential Study of the Oxidation of Copper Sulfide Minerals. *Colloids Surf. A Physicochem. Eng. Asp.* **1999**, *146*, 113–121.
128. Fan, H.; Qin, J.; Liu, J.; Liu, G.; Yang, X. Investigation into the flotation of malachite, calcite and quartz with three phosphate surfactants. *J. Mater. Res. Technol.* **2019**, *8*, 5140–5148. <https://doi.org/10.1016/j.jmrt.2019.08.037>.
129. Liu, G.; Huang, Y.; Qu, X.; Xiao, J.; Yang, X.; Xu, Z. Understanding the Hydrophobic Mechanism of 3-Hexyl-4-Amino-1, 2, 4-Triazole-5-Thione to Malachite by ToF-SIMS, XPS, FTIR, Contact Angle, Zeta Potential and Micro-Flotation. *Colloids Surf. A Physicochem. Eng. Asp.* **2016**, *503*, 34–42.
130. Liu, G.; Xiao, J.; Liu, J.; Qu, X.; Liu, Q.; Zeng, H.; Yang, X.; Xie, L.; Zhong, H.; Liu, Q. In Situ Probing the Self-Assembly of 3-Hexyl-4-Amino-1, 2, 4-Triazole-5-Thione on Chalcopirite Surfaces. *Colloids Surf. A Physicochem. Eng. Asp.* **2016**, *511*, 285–293.
131. Shen, P.; Liu, D.; Xu, X.; Jia, X.; Zhang, X.; Liu, D.; Liu, R. Effect of Ethylene Diamine Phosphate on the Sulfidization Flotation of Chrysocolla. *Minerals* **2018**, *8*, 216. <https://doi.org/10.3390/min8050216>.
132. González, G.; Soto, H. The effect of thermal treatment on the flotation of chrysocolla. *Int. J. Miner. Process.* **1978**, *5*, 153–162. [https://doi.org/10.1016/0301-7516\(78\)90012-1](https://doi.org/10.1016/0301-7516(78)90012-1).
133. Gonzalez, G.; Laskowski, J. The Point of Zero Charge of Oxidized Copper Minerals: Tenorite, Malachite and Chrysocolla. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *53*, 452–456.
134. Li, Z.; Rao, F.; Song, S.; Uribe-Salas, A.; López-Valdivieso, A. Reexamining the Adsorption of Octyl Hydroxamate on Malachite Surface: Forms of Molecules and Anions. *Miner. Process. Extr. Met. Rev.* **2019**, *41*, 178–186. <https://doi.org/10.1080/08827508.2019.1634564>.
135. Ellis, J. Analysis of accidents and incidents occurring during transport of packaged dangerous goods by sea. *Saf. Sci.* **2011**, *49*, 1231–1237. <https://doi.org/10.1016/j.ssci.2011.04.004>.
136. Singh, K.; Ihlenfeld, C.; Oates, C.; Plant, J.; Voulvoulis, N. Developing a screening method for the evaluation of environmental and human health risks of synthetic chemicals in the mining industry. *Int. J. Miner. Process.* **2011**, *101*, 1–20. <https://doi.org/10.1016/j.minpro.2011.07.014>.
137. Boening, D. Aquatic Toxicity and Environmental Fate of Xanthates. *Min. Eng.* **1998**, *50*, 65–68.
138. Young, T.L.; Greene, M.G.; Bauer, K.; Reber, N.R.; Young, S.K. Flotation of Sulfide Mineral Species with Oils. U.S. Patent 6,827,220, 7 December 2004.
139. Greene, M.G.; Walton, K.B.; Dimas, P.A.; Laney, D.G.; Young, S.K.; Young, T.L.; Reber, N.R. Collectors for Flotation of Molybdenum-Containing Ores. U.S. Patent 12/963,712, 14 June 2012.

140. Owusu, C.; Quast, K.; Addai-Mensah, J. The use of canola oil as an environmentally friendly flotation collector in sulphide mineral processing. *Miner. Eng.* **2016**, *98*, 127–136. <https://doi.org/10.1016/j.mineng.2016.08.003>.
141. Alvarez, J.; Castro, S. Flotation of Chalcocite and Chalcopyrite in Seawater and Salty Water. In Proceedings of the IV Encontro Nacional de Tratamento de Minerios, Anais, São José Dos Campos, Brazil, 2–6 May 1976; Volume 1, pp. 39–44.
142. Castro, S. Challenges in Flotation of Cu-Mo Sulfide Ores in Sea Water. *Water Miner. Process.* **2012**, 29–40.
143. Smith, L.; Heyes, G. The Effect of Water Quality on the Collectorless Flotation of Chalcopyrite and Bornite. In Proceedings of the Third International Congress on Water management in the Mining Industry, Santiago, Chile, 6–8 June 2012.
144. Jeldres, R.I.; Forbes, L.; Cisternas, L.A. Effect of Seawater on Sulfide Ore Flotation: A Review. *Miner. Process. Extr. Metall. Rev.* **2016**, *37*, 369–384.
145. Bakalarz, A.; Duchnowska, M.; Luszczkiewicz, A. *The Effect of Process Water Salinity on Flotation of Copper Ore from Lubin Mining Region (SW Poland)*; EDP Sciences: Les Ulis, France, 2017; Volume 18, p. 01007.
146. Agboola, O.; Babatunde, D.E.; Fayomi, O.S.I.; Sadiku, E.R.; Popoola, P.; Moropeng, L.; Yahaya, A.; Mamudu, O.A. A review on the impact of mining operation: Monitoring, assessment and management. *Results Eng.* **2020**, *8*, 100181. <https://doi.org/10.1016/j.rineng.2020.100181>.
147. Falagán, C.; Grail, B.M.; Johnson, D.B. New approaches for extracting and recovering metals from mine tailings. *Miner. Eng.* **2017**, *106*, 71–78. <https://doi.org/10.1016/j.mineng.2016.10.008>.
148. Gordon, R.B. Production residues in copper technological cycles. *Resour. Conserv. Recycl.* **2002**, *36*, 87–106. [https://doi.org/10.1016/s0921-3449\(02\)00019-8](https://doi.org/10.1016/s0921-3449(02)00019-8).
149. Chen, T.; Lei, C.; Yan, B.; Xiao, X. Metal recovery from the copper sulfide tailing with leaching and fractional precipitation technology. *Hydrometallurgy* **2014**, *147*, 178–182. <https://doi.org/10.1016/j.hydromet.2014.05.018>.
150. Yin, Z.; Sun, W.; Hu, Y.; Zhang, C.; Guan, Q.; Wu, K. Evaluation of the possibility of copper recovery from tailings by flotation through bench-scale, commissioning, and industrial tests. *J. Clean. Prod.* **2018**, *171*, 1039–1048. <https://doi.org/10.1016/j.jclepro.2017.10.020>.
151. Zhu, X.-N.; Nie, C.-C.; Zhang, H.; Lyu, X.-J.; Tao, Y.-J.; Qiu, J.; Li, L.; Zhang, G.-W. Recovery of high-grade copper from waste printed circuit boards by mechanical-grinding assisted flotation. *J. Clean. Prod.* **2019**, *232*, 1251–1256. <https://doi.org/10.1016/j.jclepro.2019.06.063>.
152. Garmsiri, M.R.; Nosrati, A. Dewatering of Copper Flotation Tailings: Effect of Feed Dilution on the Thickener Performance. *Miner. Process. Extr. Met. Rev.* **2019**, *40*, 141–147. <https://doi.org/10.1080/08827508.2018.1497626>.
153. Vazifeh, Y.; Jorjani, E.; Bagherian, A. Optimization of reagent dosages for copper flotation using statistical technique. *Trans. Nonferrous Met. Soc. China* **2010**, *20*, 2371–2378. [https://doi.org/10.1016/s1003-6326\(10\)60657-7](https://doi.org/10.1016/s1003-6326(10)60657-7).
154. Seaman, D.; Burns, F.; Adamson, B.; Seaman, B.; Manton, P. Telfer Processing Plant Upgrade—the Implementation of Additional Cleaning Capacity and the Regrinding of Copper and Pyrite Concentrates. In Proceedings of the 11th Mill Operators Conference, Hobart, TAS, Australia, 29–31 October 2012; pp. 373–381.
155. Van Eck, N.J.; Waltman, L. Software survey: VOSviewer, a computer program for bibliometric mapping. *Scientometrics* **2010**, *84*, 523–538. <https://doi.org/10.1007/s11192-009-0146-3>.
156. Shastri, S.; Raju, K.; Rao, K.; Rao, G. Mineral Resources and Beneficiation Plant Practices in India. *Miner. Eng.* **2000**, *14*, 1665.
157. Ruiz, J.; Lizardo, J.; Umipig, C.; Ccuno, F. The Implementation Processing Plant Modifications at Cormidom, Cerro De Maimon, Perilya. In Proceedings of the IMPC 2016: XXVIII International Mineral Processing Congress Proceedings, Quebec City, QC, Canada, 11 September 2016; Volume 4, pp. 240–250.
158. Kaya, E. Comminution Behaviour of Microwave Heated Two Sulphide Copper Ores. *Indian J. Chem. Technol.* **2010**, *17*, 455–461.
159. Azghdi, S.; Barani, K. Effect of microwave treatment on the surface properties of chalcopyrite. *Miner. Met. Process.* **2018**, *35*, 141–147. <https://doi.org/10.19150/mmp.8463>.
160. Batchelor, A.; Jones, D.; Plint, S.; Kingman, S. Increasing the grind size for effective liberation and flotation of a porphyry copper ore by microwave treatment. *Miner. Eng.* **2016**, *94*, 61–75. <https://doi.org/10.1016/j.mineng.2016.05.011>.
161. Shi, F.; Zuo, W.; Manlapig, E. Pre-concentration of copper ores by high voltage pulses. Part 2: Opportunities and challenges. *Miner. Eng.* **2015**, *79*, 315–323. <https://doi.org/10.1016/j.mineng.2015.01.014>.
162. Zuo, W.; Shi, F.; Manlapig, E. Pre-concentration of copper ores by high voltage pulses. Part 1: Principle and major findings. *Miner. Eng.* **2015**, *79*, 306–314. <https://doi.org/10.1016/j.mineng.2015.03.022>.
163. Taheri, B.; Lotfalian, M. Effect of Ultrasonic Pre-Treatment and Aeration on Flotation Separation of Chalcopyrite from Pyrite. *Iran. J. Chem. Chem. Eng. (IJCCE)* **2018**, *37*, 199–207. <https://doi.org/10.30492/IJCCE.2018.29055>.