Review

The Challenges and Prospects of Recovering Fine Copper Sulfides from Tailings Using Different Flotation Techniques: A Review

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Abstract: Flotation is a common mineral processing method used to upgrade copper sulfide ores; in this method, copper sulfide mineral particles are concentrated in froth, and associated gangue minerals are separated as tailings. However, a significant amount of copper is lost into tailings during the processing; therefore, tailings can be considered secondary resources or future deposits of copper. Particle–bubble collision efficiency and particle–bubble aggregate stability determines the recovery of target particles; this attachment efficiency plays a vital role in the selectivity process. The presence of fine particles in the flotation circuit is because of excessive grinding, which is to achieve a higher degree of liberation. Complex sulfide ores of markedly low grade further necessitate excessive grinding to achieve the maximum degree of liberation. In the flotation process, fine particles due to their small mass and momentum are unable to collide with rising bubbles, and their rate of flotation is very slow, further lowering the recovery of target minerals. This collision efficiency mainly depends on the particle–bubble size ratio and the concentration of particles present in the pulp. To overcome this problem and to maintain a favorable particle–bubble size ratio, different techniques have been employed by researchers to enhance particle–bubble collision efficiency either by increasing particle size or by decreasing bubble size. In this article, the mechanism of tailing loss is discussed in detail. In addition, flotation methods for fine particles recovery such as microbubble flotation, column flotation, nanobubble flotation, polymer flocculation, shear flocculation, oil agglomeration, and carrier flotation are reviewed, and their applications and limitations are discussed in detail.

Keywords: flotation; copper sulfides; tailings; carrier flotation; flocculation; oil agglomeration

1. Introduction

Copper (Cu), the second most produced non-ferrous metal after aluminum, has been widely used for various applications due to its unique properties such as excellent electrical and thermal conductivities, high corrosion resistance, and outstanding malleability and ductility [1,2]. The demand for Cu is projected to be continuously increasing because it is considered one of 17 materials/metals identified as critical materials/metals for realizing a low-carbon future [3,4]. Low-carbon technologies require more Cu than conventional fossil fuel-based technologies; for example, a typical 3 MW wind turbine requires 4.7 t of Cu, photovoltaic (PV) cells need ~1% Cu, and electric vehicles (EVs) use 1.7–11 times more Cu than conventional cars [3–7]. Thus, the establishment of a robust and sustainable supply chain of Cu is an important issue for humanity.
Copper sulfides are the primary source of metallic copper, which makes up 80% of the copper resources [8]. The major copper sulfide ores include chalcopyrite (CuFeS$_2$), bornite (Cu$_3$FeS$_4$), covellite (CuS), and chalcocite (Cu$_2$S). The copper concentrates from sulfide ores are usually produced by flotation and then processed by pyrometallurgical or hydrometallurgical methods to extract the copper [3,9,10].

Froth flotation is widely used to separate sulfide minerals from gangue minerals such as quartz (SiO$_2$), based on the surface properties of minerals. The principle of the flotation process is illustrated in Figure 1. In flotation, ground ore particles are suspended in water in the flotation cell and conditioned with various reagents (e.g., collector, frother, activator, depressant, and pH adjustor) to control the hydrophobicities of target and gangue minerals [11–14]. Afterward, air bubbles are induced into the pulp (mineral/water suspension), and hydrophobic copper mineral particles are attached to the bubble surface and recovered into the froth layer as a copper concentrate [15,16]. Hydrophilic gangue minerals such as quartz are not attached to air bubbles and remain in the pulp as a by-product called tailings.

Figure 1. Flotation mechanism.

Increasing demand for energy and metals around the world has led to an acute depletion of high-grade ore deposits. As ore grades decline, more challenges arise in mineral processing, including the increasing complexity of mineralogy and the decreasing grain size of mineral particles [17,18]. The first strategy to overcome the implications of complex mineralogy is to decrease the particle size in order to achieve a high degree of liberation, which produces fine to ultrafine feeds for flotation circuits. As ultrafine grinding requires a lot of energy, the second strategy includes the use of a rougher circuit for processing of coarser particles (>250 µm) followed by regrinding rougher flotation concentrates to save energy costs [19]. In either case, flotation circuits are required to process much finer or coarser feeds nowadays.

In the actual flotation process, a significant quantity of copper sulfide particles (finest and coarsest fractions) is lost in tailings, which are disposed of into the tailings storage facilities (TSFs). Since the conventional copper ores have been becoming depleted, copper tailings are gaining increasing attention as potential resources. For example, the amount of copper in TSFs is estimated to be of the magnitude of 0.13 Gt, equivalent to ~15% of the current geogenic Cu reserves [20–22]. The recovery of copper sulfides from TSFs will not only add economic value, but also protect the environment because the oxidation of copper sulfides results in the release of protons and heavy metal ions that contaminate surrounding ecosystems [23].

Efficiency of the flotation process is mainly dependent on particle size. Fine particles are unable to collide with air bubbles [24] and coarse particles are unable to attach to air bubbles; hence, they are lost into tailings. The presence of fine particles in flotation
circuits is largely the result of excessive grinding, performed to achieve a higher degree of mineral liberation.

As discussed, the tailings mostly contain the finest and coarsest size fractions. A few review papers have addressed fine and coarse particle flotation [25–29]. Some previous studies have mainly focused on the use of different types of flotation cells [18,27,28]. A detailed discussion on the development of flotation cells to address the issue of recovering fine/ultrafine and coarse particles is out of the scope of the present work. An excellent review by Hassanzadeh et al. [27,28] on this topic is recommended to the readers, while other review articles have mainly focused on flotation kinetics [25,26,29]. However, to the best of our knowledge, there is a lack of thorough review on the comparison of different flotation techniques with a focus on the recovery of fine copper sulfides from tailings.

Therefore, the present article reviews the application of different flotation techniques to recover fine copper mineral particles from tailings. In the first part of this review paper, the mechanism of tailing loss is discussed in detail. After this, different flotation techniques such as column flotation, microbubble flotation, nanobubble flotation, polymer flocculation, shear flocculation, oil agglomeration, and carrier flotation are reviewed, and their applications on tailings and limitations are discussed in detail. This review aims to provide researchers who are working in the area of mineral processing with rough information about fine particle flotation, and shed some light on developed flotation techniques for fine particle separation from tailings.

2. Tailing Loss

2.1. Tailing Amount

Tailings from the flotation process account for ~98% of total ore fed to the concentrator and are usually stored in large tailing dams near the mine [30]. Flotation tailings are termed as the rejected product of the flotation process, and according to the reported literature data, 90–95% of plant tailings are produced from the flotation process [31–33]. Flotation tailings mainly contain gangue minerals, while a significant amount of valuable copper sulfide particles is also contained. As shown in Table 1, it has been reported that around 10–20% of copper in the ore is lost in the tailings. The copper grade in the tailings is 0.04–0.2%, which is very low in comparison with standard copper ores containing over 0.5% of copper. Because of this, low-grade tailings are not considered an economically valuable copper source at present; however, when copper demand increases and methods to recover copper from tailings are developed, tailings can be considered as a secondary deposit or future resource of copper.

2.2. Mechanism

The main operation of copper mineral processing is generally composed of two steps: (i) comminution to liberate valuable copper minerals from non-valuable gangue minerals, and (ii) flotation to separate copper minerals from gangue minerals. After flotation, copper concentrates are sent to the smelter for the production of highly purified copper cathodes (>99.99% Cu), while tailings are disposed of in tailing dams near mine sites.

In an ideal mineral processing of copper ores, all copper mineral grains must be liberated from gangue minerals in the comminution step (crushing and grinding) before separation. In an actual comminution step, perfect liberation is difficult because the process consumes a lot of energy and generates excessively fine particles, which cannot be recovered in the separation step [34]. Because of these reasons, as shown in Figure 2, actual ground ores are a mixture of liberated (fine) copper mineral and gangue grains, and unliberated (coarse) copper minerals locked with gangue minerals.
Table 1. Industrial flotation data from copper concentrators [30].

<table>
<thead>
<tr>
<th>Concentrator</th>
<th>Ore Treated, Tonnes/Year</th>
<th>Concentrate, Tonnes/Year</th>
<th>Cu Recovery to Concentrate, %</th>
<th>Cu Loss to Tailings, %</th>
<th>Tailings Grade, % Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>El Soldado, Chile</td>
<td>7,700,000 (2010)</td>
<td>67,000</td>
<td>-</td>
<td>-</td>
<td>0.18</td>
</tr>
<tr>
<td>Los Bronces, Chile</td>
<td>20,500,000 (2010)</td>
<td>676,000</td>
<td>-</td>
<td>-</td>
<td>0.133</td>
</tr>
<tr>
<td>Africa (open Pit)</td>
<td>4,000,000</td>
<td>35,000</td>
<td>80</td>
<td>20</td>
<td>0.018</td>
</tr>
<tr>
<td>Africa (under ground)</td>
<td>900,000</td>
<td>21,000</td>
<td>85</td>
<td>15</td>
<td>0.04</td>
</tr>
<tr>
<td>Mantos Blancos Chile (open pit)</td>
<td>4,500,000</td>
<td>125,000</td>
<td>89</td>
<td>11</td>
<td>0.12</td>
</tr>
<tr>
<td>Cerro Verde, Peru</td>
<td>39,000,000</td>
<td>750,000</td>
<td>88</td>
<td>12</td>
<td>0.075</td>
</tr>
<tr>
<td>Sierrita, USA</td>
<td>37,000,000</td>
<td>325,000</td>
<td>84.3</td>
<td>15.7</td>
<td>0.041</td>
</tr>
<tr>
<td>Ray, USA</td>
<td>10,000,000</td>
<td>150,000</td>
<td>90</td>
<td>10</td>
<td>0.035</td>
</tr>
<tr>
<td>Dexing, Jiangxi Province, China</td>
<td>13,500,000</td>
<td>150,000</td>
<td>85.5</td>
<td>14.5</td>
<td>0.084</td>
</tr>
<tr>
<td>Baiyin, Gansu Province, China</td>
<td>3,600,000</td>
<td>46,000</td>
<td>83</td>
<td>17</td>
<td>0.28</td>
</tr>
<tr>
<td>Hujiayu, Shanxi Province, China</td>
<td>750,000</td>
<td>6800</td>
<td>96.05</td>
<td>3.95</td>
<td>-</td>
</tr>
<tr>
<td>Fenghaungshan, Anhui Province, China</td>
<td>600,000</td>
<td>7200</td>
<td>93.62</td>
<td>6.38</td>
<td>0.084</td>
</tr>
</tbody>
</table>

Figure 2. Illustration of an ore fragment (mineralization in dark red) and the products of comminution: (1) highly liberated particle, (2) poorly liberated or gangue-rich particle, (3,4) moderately liberated particles (middlings), (5) liberated fine mineral particles, and (6) fine gangue particles.

In the separation process, the behavior of unliberated grains depends on the copper mineral portion in the grain; that is, when the copper portion is large, an unliberated particle may act as a (liberated) copper mineral; when the copper portion is small, it may behave as gangue mineral. Because of this, a part of copper minerals in unliberated grains is lost into tailings together with gangue minerals. This is one of the reasons (mechanisms) for copper loss in the tailings.

Another case of copper loss occurs even for fine liberated particles during separation using flotation. In flotation, mineral particles suspended in water collide and attach to air bubbles induced into the flotation cell, and then they float to the surface of the water as a froth product. The flotation efficiency of mineral particles depends on particle size. Research on the relationship between particle size and floatability began in the early 1930s in work presented by Gaudin et al. (1931) [35], which showed that coarse and fine particles are more difficult to recover than intermediate-sized particles. In the case of chalcopyrite flotation, it has been reported that copper recovery to the froth was around 95% at particle sizes of 10–150 μm, while the recoveries decreased to 50% when particle size decreased from 20 μm to 3 μm [26,36]. The flotation process is more efficient in the particle size...
range of approximately 10–100 µm [24,37,38], and it is usually poor with an increased percentage of ultrafine particles (<10 µm) in the system [39–41]. The majority of copper lost into flotation tailings at operating concentration plants occurs for particle sizes smaller than 20 µm and larger than 105 µm. In general, liberating particles can be increased by decreasing particle size (which increases mineral surface area) [42]. In flotation, a particle’s lower size limit varies for different minerals [39], and some studies have reported good recovery of ultrafine particles [24,43]. Michael et al. [35] reported the effects of particle size on the distribution of copper to froth and tailings during conventional flotation. Recoveries of copper to froth were maximum at particle sizes between 30 and 150 µm, with a distinct drop in recovery outside of this range, resulting in a loss of ultrafine and coarse particles into tailings (Figure 3). It is evident from Figure 3 that a substantial amount of valuable minerals is lost into the tailings in both the finest and coarsest fractions. The reason for the dependence of flotation efficiency on particle size is described below.

\[
P = P_c \times P_a \times (1 - P_d)
\]

Figure 3. Conventional flotation data for industrial sulfide flotation circuits [44].

In flotation, air bubbles are injected into a mineral particle/water suspension, which rise by buoyancy and collide with suspended mineral particles. If the particle is hydrophobic, it is stably attached to air bubble and is not detached from the bubble. This captured particle is then floated with air bubbles and recovered as a froth product.

Figure 4 illustrates the process of particles being captured by a rising air bubble. The probability of particles \( P \) being captured by bubbles during the flotation process in the cell can be expressed as follows [40,45]:

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\[
P = P_c \times P_a \times (1 - P_d)
\]

where \( P_c \), \( P_a \), and \( P_d \) represent the probabilities of collision, attachment, and detachment, respectively (Figure 4). The collision between fine particles and the rising bubbles in mechanical flotation cells becomes poor because of the smaller mass and low momentum of fine particles [24,46–48]; fine particles follow fluid streamlines around the bubble.
Collision efficiency is linked with the size ratio of the mineral particle and air bubble. 

\[ P_c = A \left( \frac{D_p}{D_b} \right)^n \]  

(2)

where \(D_p\) and \(D_b\) represent the diameters of particle and bubble, respectively, and \(A\) and \(n\) are empirical flow regime constants.

Attachment probability \((P_a)\) and detachment probability \((P_d)\) are mainly functions of the particle surface properties. For hydrophobic minerals such as chalcopyrite, the values of \(P_a\) and \(P_d\) could be assumed to be 1 and 0, respectively. In this case, \(P\) is mainly dependent on \(P_c\). Based on Equation (2), the collision probability \((P_c)\) is directly proportional to the particle to bubble diameter ratio. With a significant decrease in the diameter of particles \((D_p << D_b)\), the collision probability is substantially decreased, which explains the very low recovery rates of fine particles. For excessively coarse particles, collision probability \((P_c)\) is high; however, attached particles are easily detached from air bubbles by turbulent flow, i.e., \(P_d\) is high \([49–51]\). This is because of the relatively small specific surface area of coarse particles, which reduces particle–bubble attachment strength. This is one of the reasons for the low flotation recovery of coarse particles into the froth. Moreover, because of poor suspension and low dispersion of coarse particles, particle–bubble collision efficiency is limited, which reduces the flotation kinetics rate and final recovery.

As discussed above, there are two major reasons for tailing loss of copper in the flotation process: (i) tailing loss of ultrafine particles due to the excessively low collision efficiency between particles and air bubbles in flotation cells; and (ii) coarse unliberated
copper minerals associated with gangue minerals, which are easily detached from an air bubble in flotation.

For recovering copper from tailings, regrinding is needed to liberate copper minerals from locked grains. As a result, liberated but fine copper mineral particles are formed. This necessitates the development of flotation techniques to recover fine copper mineral particles from tailings. Numerous flotation methods have been developed to enhance particle–bubble collision efficiency and improve fine particle recovery either by increasing the particle size or decreasing the bubble size [43,52]. In the following sections, these techniques are reviewed concerning their applications towards tailings, which contain mostly fine mineral particles.

3. Methods for Copper Recovery from Tailings
3.1. Decreasing Bubble Size Approach

3.1.1. Column Flotation

The column flotation cell (CFC) was invented in the 1960s but did not gain wide acceptance in the processing of base metals until the early 1980s [28]. In column flotation, ore is introduced near the top of the column and sparging air from bottom, creating a deep froth zone. Wash water is added from the top to remove fine entrained particles [53]. Flotation circuits use multiple flotation cells in series to recover the maximum amount of desired minerals. Circuits consist of a set of cells called rougher, cleaner, and scavenger, as illustrated in Figure 5. Rougher flotation cells are usually mechanical type and appear first in the circuit, to increase the recovery of the valuable minerals. To minimize valuable mineral loss from final tailings, tailings from rougher cells are fed to scavenger cells, and the froth from the rougher cells is reground to liberate the middlings. This product is then fed to the cleaner cells. For cleaner flotation, column-type flotation cells that produce smaller bubbles than mechanical flotation units are frequently used [54,55]. By using smaller bubbles, the collision efficiency of particles and bubbles increases, resulting in higher copper recovery for fines in column flotation.

![Figure 5. A simplified flotation circuit.](image)

The size of air bubble in the column flotation cell depends strongly on the bubble generator/sparger. Different types of bubble generators/spargers are used in column flotation. Depending on the technique used to create the bubbles, there are three types of spargers. In one type, the air is pumped into a porous material, such as rubber or cloth, to produce bubbles. However, such spargers have durability issues (wear and tear), pore blockage by particles, and difficulties in consistently maintaining optimal bubble
size. In the jetting type, air and water are forced through a small circular opening at high pressure [54,56]. Lastly, the sparger type utilizes the shearing motion of a slurry-air mixture to generate fine bubbles after passing through a specially designed tube [56].

An in-line mixer bubble generator produced relatively large bubbles up to a diameter of 0.35 mm, according to laboratory studies [57]. In a comparison of Microcel™ and jet-type spargers, it was found that the former produced smaller bubbles, thereby increasing the recovery [58]. However, the mean diameter of bubbles produced by these two types of spargers (1–3 mm) is still relatively large. Considering this, according to Equation (2), for particles with a size <10 µm, the ideal bubble size is <150 µm.

The advantages of these devices include minimal installation costs, low operating costs, and the ability to produce significantly higher-grade concentrates than conventional cells. Even though column cells have been successful in industrial installations, they still have two inherent flaws. The first problem is that coarse particles have high settling velocities, leading to a shorter residence time in the cell, making them hard to recover. Furthermore, fine particles generally do not possess enough inertia to overcome the streamlines around bubbles and are less likely to collide with them [59].

### 3.1.2. Microbubble Flotation

As already discussed in the above section, one of the possible ways to overcome the difficulties associated with fine-particle flotation is to reduce bubble size to a few micrometers. Microbubbles are defined as air bubbles with a diameter range of 1–100 µm [60,61]. To generate microbubbles, several techniques are used (Table 2), e.g., electro-flotation, dissolved-air flotation, hydrodynamic cavitation, and dispersed-air flotation. Electro-flotation (or electrolytic flotation) has good controllability of bubble size, but it is more suitable for small-scale applications due to its low throughput and high energy consumption [62–64]. Due to microbubble stability problems in agitated flotation cells, microbubble flotation is primarily carried out in column-type flotation cells [65]. Laboratory experiments were performed using this technique to recover copper, zinc, and lead from a complex sulfide ore of <5 µm size [60,66].

Even though microbubble flotation is promising, it has several drawbacks [25]. When the bubbles are too small (<200 µm), their collision efficiency with fine particles is high, however, they will float too slowly due to their low buoyancy. On the other hand, if bubbles are large (>500 µm), they will float fast; however, they have low collision efficiency with fine particles [67]. Due to the slow speed of the microbubbles rising with attached mineral particles, longer residence times are required in the flotation circuit. Furthermore, the microbubbles cause a higher water recovery, thereby increasing gangue mineral entrainment, which reduces the selectivity [39,68].

### Table 2. Studies on the use of microbubbles in flotation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Minerals Studied</th>
<th>Process/Effects</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electroflotation</td>
<td>Chalcopyrite (&lt;20 µm)</td>
<td>Bubble generation by electrolysis. Improved recovery by electrolytic oxygen.</td>
<td>[69]</td>
</tr>
<tr>
<td>Charged microbubble/colloid gas apohrons (CGAs) microbubble</td>
<td>CuO and SiO$_2$ (&lt;10 µm)</td>
<td>CGAs generated using high speed impeller. The grade of CuO improved from 59% to 82%. Recovery of CuO improved from 58% to 77%.</td>
<td>[70]</td>
</tr>
</tbody>
</table>
Table 2. Cont.

<table>
<thead>
<tr>
<th>Name</th>
<th>Minerals Studied</th>
<th>Process/Effects</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microbubble flotation</td>
<td>Pyrite (FeS$_2$), chalcopyrite (CuFeS$_2$), galena (PbS), and sphalerite (ZnS)</td>
<td>Bubbles generated using Silica Porous Glass (SPG) filter.</td>
<td>[66]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Microbubble flotation of ultrafine sulfide minerals.</td>
<td></td>
</tr>
<tr>
<td>Microbubble flotation</td>
<td>Galena (PbS) and sphalerite (ZnS)</td>
<td>Bubbles generated using Silica Porous Glass (SPG) filter.</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Collector-less microbubble flotation using sodium hydrosulfide.</td>
<td></td>
</tr>
<tr>
<td>Nano-microbubble</td>
<td>Chalcopyrite fines (14–38 µm)</td>
<td>Bubble size ($D_{90} = 100$ µm) generated by hydrodynamic cavitation.</td>
<td>[72]</td>
</tr>
<tr>
<td></td>
<td>Ultrafine particles (5–14 µm)</td>
<td>Improved recovery of fine and ultrafine particles (16–21%).</td>
<td></td>
</tr>
</tbody>
</table>

3.1.3. Nanobubble Flotation

Flotation of fine particles can be enhanced by nanobubbles. Parker et al. were the first to propose nanobubbles to improve the flotation of fines [73]. Nanobubbles (NBs), also called ultrafine bubbles, are gas cavities with a diameter of <1 µm [74–76]. As shown in Figure 6, nanobubbles are adsorbed on fine mineral particles when they are pre-treated with them, forming nanobubble–particle aggregates and, thus, increasing the apparent particle size and improving collision efficiency [77–79]. In addition to enhancing the fine particle hydrophobicity and forming aggregates, NBs also act as secondary collectors [80–82].

![Figure 6. Schematic mechanism of nanobubble flotation](reprinted with permission from Li et al. [83], copyright (2022) Elsevier).
NBs are produced by different methods such as hydrodynamic cavitation, gas over-saturation, power ultrasound, electrolysis, chemical reaction, solvent exchange, temperature exchange, and membrane modules [83,84]. The generation of NBs is a complex physicochemical process influenced by several factors, including temperature, electrolyte concentration, dissolved gas concentration in solution, and the type and concentration of reagents [84–90]. Studies have shown that nanobubbles can significantly boost process efficiency by enhancing coarse bubble attachment onto adhered NBs and by aggregating the problematic fine particles [72,77,80,89,91]. The NBs are considered to have significant potential in mineral processing due to the better recovery of ultrafine particles [92].

Flotation kinetics and recovery are reportedly higher for a fine fraction (<38 µm), while the grade and selectivity index tend to be higher for coarse size fraction (<150 µm) [93]. Ahmadi et al. [72] confirmed that the flotation recovery of fine (14–38 µm) and ultrafine (5–14 µm) chalcopyrite particles with NBs increased by approximately 16–21%. With surfactants (collector and frother), nanobubbles may cause a decrease in grade, primarily due to increased entrainment [93,94]. Nanobubbles should be used in the rougher and scavenger stages, where recovery is of primary importance, while the cleaner stage mainly controls the grade. Optimizing the hydrodynamic conditions and surfactant types is required to reduce the amount of water recovery associated with NBs, which will reduce the entrainment rate [94].

3.2. Increasing Particle Size Approaches

Theoretically and experimentally, it has been observed that the flotation rate elevates when the particle size is large [39,95–99]. As mentioned above, the agglomeration of fine mineral particles can be an effective method for improving collision efficiency between mineral particles and air bubbles during flotation. The recovery of fines by using this approach has been studied extensively, and several techniques have been developed. These techniques mainly include polymer flocculation, shear flocculation, oil agglomeration, and carrier flotation. Table 3 provides a brief overview of these techniques, and Figure 7 presents a schematic diagram of the governing mechanisms.

<table>
<thead>
<tr>
<th>Method</th>
<th>Reagents and Material</th>
<th>Types of Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer flocculation</td>
<td>Polymer, surfactant</td>
<td>Hydrophobic, chemical, hydroxyl functional group, electrostatic</td>
</tr>
<tr>
<td>Shear flocculation</td>
<td>Surfactant</td>
<td>Hydrophobic interaction</td>
</tr>
<tr>
<td>Oil agglomeration</td>
<td>Oil, surfactant</td>
<td>Capillary forces</td>
</tr>
<tr>
<td>Carrier flocculation</td>
<td>Surfactant, carrier material</td>
<td>Hetero coagulation, hydrophobic interaction</td>
</tr>
</tbody>
</table>

3.2.1. Polymer Flocculation

In flocculation, organic polymers with a high molecular weight (>1 million) are used to form a molecular bridge between particles [100–102]. A polymer induces flocculation of mineral particles by attaching itself to two or more particles, bridging the particles. If polymers are adsorbed on a specific mineral surface, selective flocculation occurs [103,104]. Selective flocculation is usually divided into feed preparation, selective adsorption of flocculant (polymers) on specific minerals, floc formation, and conditioning. For separating flocs from dispersed particles, flotation or sedimentation can be used [104].
Usually, flocculation is possible with a small amount of flocculant. This is an advantage of the flocculation technique, in comparison with other techniques discussed below. However, selective flocculation has proven to be a challenging technique [104]. Cellulose-type compounds are typical flocculants, and their effects on the flocculation of ground chalcopyrite, pyrite, and quartz were investigated using silylated cellulose nanofibers (SiCNF) [105]. The results showed that all minerals are flocculated in the presence of SiCNF, suggesting that cellulose-type compounds cannot be used for the selective flocculation of typical copper ores containing chalcopyrite, pyrite, and quartz. In another study [106], synthesized polymer xanthate was used as a flocculant before the flotation of complex sulfide ores, demonstrating good recovery. However, the grade of the concentrate was very low, indicating that the flocculant was non-selective.

3.2.2. Shear Flocculation

Shear flocculation is a technique to improve flotation kinetics. Mineral particles suspended in water have an electrical surface charge, and this causes a repulsive energy barrier between the homogeneously charged particles, suppressing their flocculation. In shear flocculation, kinetic energy is mechanically imparted to hydrophobic particles to make them collide together, in a mechanical mixing tank. High intensity stirring of hydrophobic mineral particles overcomes the energy barrier causing repulsion due to homogeneously charged particles [57,107,108]. Warren initially proposed this technique [108], concluding that, subject to provision of sufficient kinetic energy to the system, using agitation overcomes the energy barrier, forming flocs/aggregates of hydrophobic particles. Warren proposed that shear flocculation occurs in three steps: (1) in the turbulent movement, the average collision energy is much higher than thermal energy, which allows colloidal particles to approach each other; (2) the formation of flocs/aggregates is preferred with the energy of a “hydrophobic bond” in the event of a collision in direct contact between hydrophobic particles; (3) the resistance to the thinning and removal of the water layers separating the approaching particles is likely less in the case of hydrophobic particles than with colliding hydrophilic particles [109].

In a study conducted by Tabosa et al. [52], it was observed that high-intensity conditioning had less effect when the particle size of copper particles was less than 15 μm.
However, for particle sizes >15 \( \mu \text{m} \), high-intensity conditioning increased copper recovery. The flotation of galena or sphalerite with a particle size less than 20 \( \mu \text{m} \) after shear flocculation has been reported [110]. Over 80% recovery was obtained for both galena and sphalerite when shear flocculation was applied. Shear flocculation also requires a precise control of the hydrodynamics of the system. In the flocculation process, there is a fine balance between the amount of shear force that initiates the process and the amount of shear that disintegrates aggregates beyond a certain point. Currently, shear flocculation is not frequently used in mineral processing, despite its potential. This may be due to the difficulty in controlling shear flocculation, selectivity issues, and high energy demands.

3.2.3. Oil Agglomeration

The oil agglomeration technique was developed in the early 1920s for coal cleaning; it has been modified and improved many times since then [111]. This technique uses oil as a bridging liquid to aggregate minerals [46–48,112,113]. Kerosene, vegetable oil, and diesel oil are used as bridging liquids for agglomeration to increase apparent particle size, leading to improved flotation of ultrafine particles [114]. The capillary force of the bridging liquid between particles causes an attraction force between particles [111]. The application of this technique has been researched for the purification of coal [111,115–121], recovery of gold [122,123], molybdenite [114], and chalcopyrite [46–48].

Dosage and type of oil, hydrophobicity of minerals, and agitation strength are the key parameters for oil agglomeration [117,124–127]. Oil is expensive and required in large amounts, which need to be reduced to improve economic viability. This is a major disadvantage associated with oil agglomeration for industrial-scale operations [112].

To reduce the amount of oil used in the agglomeration, the use of oil–water emulsions has been proposed [112]. Using emulsifiers decreases oil droplet size and increases the surface area [128–130]. In a recent study [46], emulsified oil agglomeration flotation was conducted on a fine chalcopyrite/quartz mixture by varying different parameters: agitation strength, collector dosage, and amount of oil. Emulsified oil agglomeration flotation significantly improved copper (Cu) recovery from around 45% without agglomeration to over 80% with agglomeration, as well as separation efficiency from around 30% without agglomeration to 70% with agglomeration.

It was observed that strong agitation strength is required to produce a large number of oil droplets, which is important for producing a larger agglomerate of mineral particles. However, this process consumes a lot of energy, making it expensive and difficult to incorporate into flotation circuits. Later, a new method was developed to overcome this problem by using emulsified oil stabilized by a surfactant to produce a stable oil–water emulsion that does not require strong agitation strength [47]; this method can be easily integrated into the existing flotation circuits.

A major problem of oil agglomeration is the amount of oil and high agitation speed required. This problem can be overcome when emulsified oil is used: small oil droplets become stable [131], and strong agitation is not needed. However, when the number of copper minerals becomes smaller, agglomerate size becomes small, and the flotation rate is low. Therefore, it is difficult to use oil agglomeration for Cu recovery from tailings with a very minute amount of copper mineral particles (Figure 8).

3.2.4. Carrier Flotation

Carrier flotation is a method for improving fine particle recovery in flotation. In this method, coarse carrier particles are added to the flotation cell and agitated together with fine mineral particles. The fine particles are then attached to the surface of coarse carrier particles and floated together.
The carrier flotation technique was initially developed to remove impurities from kaolin clay, using coarse limestone as a seed or carrier [132]. Normally, coarse particles are present in the ore, so adding extra coarse particles is not desirable in that case. If coarse particles are already present, they may act as a seed, in which case introducing extra carrier particles may not work [132,133]. When fine particles are attached to coarse particles (carrier or seed) of the same mineral, the process is termed autogenous carrier flotation [134]. Heterogenous carrier flotation uses coarse carrier particles that are different from the target fine minerals. Autogenous carrier flotation was first carried out on wolframite [135], and later used for coal [136]. With heterogeneous carrier flotation, numerous research works have been reported. For example, Jorge Rubio and Heinz used polypropylene treated with oleic acid as a carrier for different minerals [137].

Requirements for carrier flotation are the presence of coarse particles (carrier or seed), and hydrophobic coarse and fine particles [107]. The collision rate between fine and coarse particles is comparatively greater than fine and fine particles; also, fine particles attach well to the surface of coarse particles [134,138–140]. The schematic mechanism of carrier flotation is presented in Figure 9. It can be seen that when coarse carrier particles are agitated together with fine mineral particles, the fine particles are selectively attached to the surface of carrier particles.

Figure 8. Application of agglomeration to flotation circuit.

Figure 9. Schematic mechanism of carrier flotation.
In carrier flotation, agitation time and intensity; pulp density; carrier particle size; coarse–fine particle ratio; and chemical factors such as pH, collector dosage, the extent of hydrophobicity, the surface charge of the particle, and geometry of the cell are important variables, affecting the recovery of fines. Among these variables, the coarse–fine ratio may be the most important.

When the carrier (coarse particle) amount is increased, fine particle recovery is also increased [139]. However, overly large amounts of coarse particles are harmful. If the amount of coarse particles is too large, collision rates between coarse particles become high, which may cause detachment of already adhered fine particles [107].

In a study by Li et al. [141], interactions between coarse and fine hematite particles were studied. When the amounts of coarse and fine hematite particles were equal, attachment of fines to coarse carrier particles was maximized, causing maximum flotation recovery of fines.

It has been reported that carrier flotation is an effective method for improving the recovery of fine copper grains, where researchers investigated the autogenous carrier flotation technique using coarse chalcopyrite particles [142]. The fine chalcopyrite recovery was improved from 25% without a carrier to 80% with a carrier. The particle size distribution results as well as extended Derjaguin–Landau–Verwey–Overbeek (EDLVO) calculations confirmed the attachment of fine particles to coarse carrier particles.

As already discussed, considering tailings as future deposits, polymer flocculation, oil agglomeration, and shear flocculation are difficult to apply to copper recovery from tailings. This is mainly because of the low copper grade in tailings: floc/aggregate size depends on the number of copper minerals, and the size is limited when the amount of copper mineral is small.

Tailings consist primarily of gangue minerals, with a minute amount of valuable/target minerals, so the above-mentioned methods are unlikely to efficiently recover fine minerals from tailings. On the other hand, in carrier flotation, aggregate size is mainly dependent on the carrier size. This gives carrier flotation (autogenous carrier flotation) an advantage over other mentioned techniques (polymer flocculation, shear flocculation, and oil agglomeration) for recovering fine particles from tailings. However, an alternate carrier is required because of the non-availability of coarse chalcopyrite particles at the tailings site. Pyrite may be a good choice because of its abundance and availability at mine sites. The effectiveness of pyrite as a carrier for finely ground chalcopyrite particles was recently reported by Bilal et al. [143]. In this study [143], Cu²⁺-activated pyrite particles were used as the carrier for recovering finely ground chalcopyrite particles. The wet sieving method (using ethanol spraying) was used to separate fine fractions from coarse fractions. However, when integrating this method into existing flotation circuits on an industrial scale, a post-flotation method was still not proposed. Therefore, the development of a post-flotation process to separate attached fine copper minerals from carriers (Cu²⁺-activated pyrite) is needed.

4. Summary

In mineral processing at copper mines, around 10–20% of copper is lost into tailings. This is mainly because of the presence of overly fine copper mineral particles and unliberated copper mineral particles, which cannot be recovered in flotation. To recover copper from tailings, regrinding is required to liberate locked copper mineral particles, producing fine grains. This necessitates the development of flotation techniques to recover fine copper minerals from tailings. To this end, the present review addresses the challenges and prospects of recovering fine copper sulfides from tailings using different flotation techniques. Several techniques have been developed to recover fine mineral particles either by increasing particle size or by decreasing bubble size. The following findings are highlighted:

- Evaluating literature data shows that to recover fine particles and to maintain the required particle–bubble diameter ratio, bubble size needs to be reduced or particle size needs to be increased.
• The mean diameter of bubbles produced in column cells (1−3 mm) is still relatively large, and fine particles are less likely to collide with rising bubbles.

• In addition to enhancing fine particle recovery by forming aggregates, NBs also act as secondary collectors, thereby reducing collector and frother consumption.

• Microbubbles rising with attached mineral particles lead to longer residence times in the flotation circuit due to their slow speed. Moreover, the microbubbles increase water recovery, thereby increasing gangue mineral entrainment and reducing selectivity.

• Polymer flocculation is a promising method for increasing the apparent particle size, but this method is less selective.

• Shear flocculation requires a comparatively high amount of energy compared to other aggregation methods.

• Oil agglomeration requires a large amount of oil and agitation strength; however, this problem can be overcome when emulsified oil stabilized by a surfactant is used.

• Carrier flotation utilizes hydrophobic interactions, and fine particles are selectively attached onto the surface of coarse carrier particles.

• Polymer flocculation, shear flocculation, and oil agglomeration can generate larger flocs/aggregates from fine particles, thereby improving fine particle recovery. However, none of these techniques can be applied to recovering copper from tailings because the amount of copper minerals in tailings is small, causing a limitation of floc.aggregate size. Their applicability in mineral flotation has also been limited due to the lack of selectivity in aggregation.

• Carrier flotation is more suitable for copper recovery from tailings because agglomerate size is mainly dependent on carrier size itself, and can be applied even if the amount of fine particles is limited.

In light of the above conclusions and given information in the literature, the following future studies are recommended:

• Microbubble flotation and nanobubble flotation can improve the flotation rate and recovery of fine particles; however, they cause a higher water recovery, which causes increased entrainment of gangue minerals. Researchers have rarely addressed NB’s impact on grade, separation efficiency, and selectivity of separation. More research is needed in this regard.

• The size of the agglomerate depends on the number of valuable mineral particles available in the feed. This gives the carrier flotation an advantage over the other agglomeration techniques because, in carrier flotation, agglomerate size is decided by the carrier itself; however, all these techniques have been applied on high-grade ores. The efficiency of these methods needs to be checked on real samples, i.e., tailings and low-grade ores.

• Autogenous carrier flotation can be integrated into the existing flotation circuits to minimize the loss of fine copper mineral particles, but the amount of carrier particles needs to be optimized for industrial scale operations.

• Research has shown that Cu²⁺-activated pyrite can be used as a carrier; however, there is no study on the post-flotation separation of fine particles attached to Cu²⁺-activated pyrite particles. Therefore, further studies are recommended in this regard.

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