Biobeneficiation of PGMs

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Conventional beneficiation of the Platinum Group of Metals (PGMs) relies on the use of inorganic chemicals. With the depreciation of high grade deposits, these conventional processes are becoming less economically viable. Furthermore, the use of chemicals has serious negative impacts on the environment. To address the challenges of conventional PGM beneficiation, biobeneficiation has been proposed. Bio-beneficiation is the concentration of mineral species by employing microorganisms that interact with either the gangue or the valuable mineral species. Bio-beneficiation can also be described as the use of microorganisms to interact with minerals to subsequently induce processes such as magnetic separation, flotation, and flocculation.

Keywords: bioprocessing ; PGMs ; base metal sulphides ; bioflotation ; bioflocculation

1. Typical Beneficiation Process of PGMs

Froth flotation is a physico-chemical process whereby mineral particles are separated based on their affinity for an air environment. Particles with a high affinity for an air environment (hydrophobic) will attach to rising bubbles and float to the froth phase, thus being separated from the particles that have an affinity for water molecules (hydrophilic). During flotation, a slurry is fed into an agitated and aerated tank where the separation process takes place, resulting in two products, concentrate and tailings.

Froth flotation began in 1905, when Haynes used the technique to separate sulphides from gangue using oil [1]. The sulphide mineral particles have different surface properties from those of the gangue, leading to the preferential coating of gangue by oil in Haynes' work. The immiscibility of oil and water in turn results in the selective flotation of the oil-coated sulphide minerals. It is against this foundation that several reagents, which will be discussed in the subsequent sections, have been developed to enhance the selectivity of froth flotation. Factors that influence froth flotation will be discussed in the subsequent sections; however, at this juncture it is important to note that an optimum particle size is required for effective flotation. Therefore, froth flotation typically follows the comminution stage, and an example of a flow sheet encompassing both comminution and flotation is shown in **Figure 1**. Prior to flotation, the runoff mine (ROM) feed undergoes closed-circuit milling using a hydrocyclone as a classifier. The hydrocyclone product (undersize) undergoes various flotation stages to maximize both grade and recovery. Recovery is maximized in the rougher stages, whereas grade is maximized in the cleaner stages.

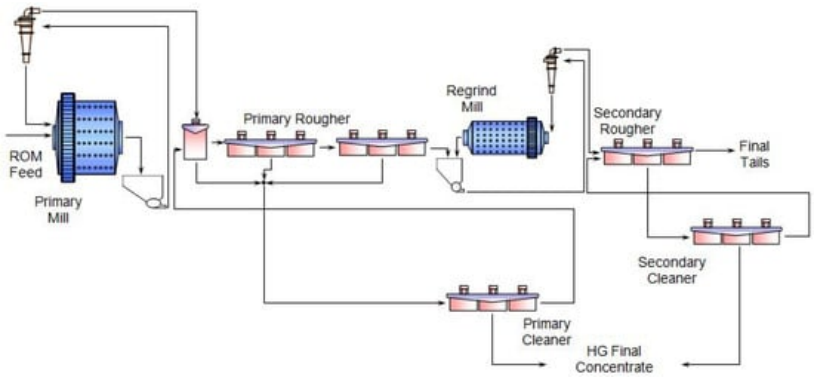

Figure 1. Typical concentration plant for the processing of PGMs, adapted from Engelbrecht [2].

As mentioned above, to create the optimum chemical conditions for effective separation of particles, flotation reagents are usually added. These reagents are classified as frothers, collectors and regulators. The flotation reagents help a mineral species to be selectively floated or not floated. Naturally, certain minerals such as coal, talc, graphite, diamond and molybdenite possess the physico-chemical properties to be separated without the addition of reagents. Sulphide minerals are rendered hydrophobic by the addition of xanthate collectors. Because (as mentioned earlier) PGMs tend to exist within

base metal sulphide minerals [3], it is therefore possible to recover PGMs using flotation and to separate them from the non-floating silica or chromite gangue.

The interaction of mineral particles with flotation reagents is influenced by the surface potential (zeta potential). A positive zeta potential attracts anions, and the opposite is true for a negative zeta potential. For flotation to take place, the surface potential of mineral particles must therefore be opposite to the charge of the flotation reagents. However, the surface potential depends on pH, whereby an alkaline pH creates negative zeta potentials on mineral particles, while the opposite is true under acidic conditions. A typical relationship between pH and zeta potential is shown in **Figure 2** [4]. Therefore, the hydrophobicity or hydrophilicity of particles is indirectly influenced by the pH of the pulp phase. The combined effects of pH and collector concentration in the flotation of some sulphide minerals is shown in **Figure 3** [5]. For each mineral species in **Figure 3**, flotation occurs at the conditions to the left of the corresponding curve. Generally, bioflotation uses microorganisms as depressants and conventional chemical collectors are used to render hydrophobicity to the undepressed species of interest [6][7][8][9]. In these cases, where microorganisms serve as depressants only, they help to enhance the effectiveness of the conventional collectors by selectively depressing some of the unwanted minerals.

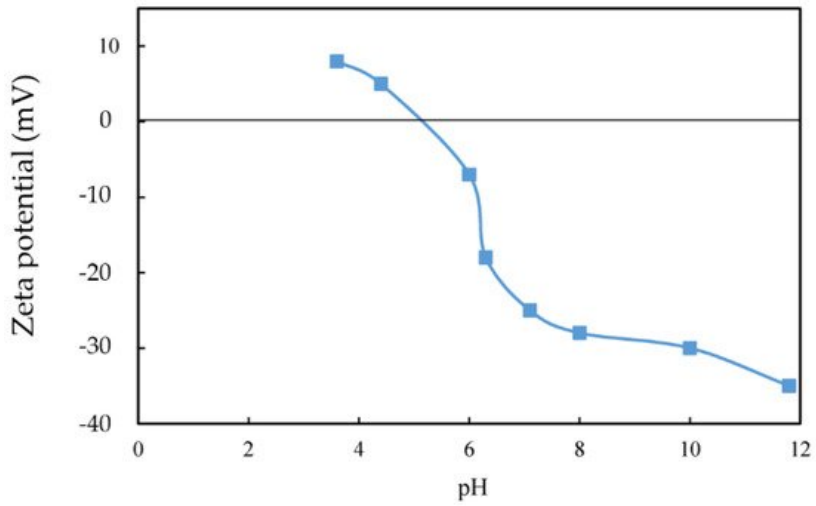

Figure 2. Zeta potential as a function of pH, adapted from Filippov et al. [4].

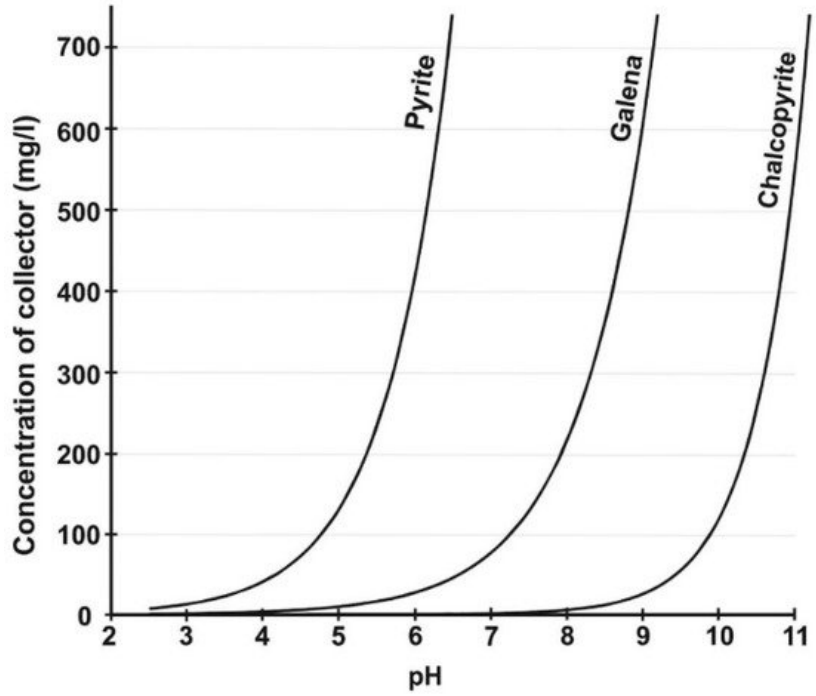

Figure 3. The effect of collector concentration and pH value in the flotation of chalcopyrite, pyrite and galena, adapted from Wark and Cox [5].

The purpose of frothers is to ensure that a stable froth is achieved so that, as much as possible, the minerals attached to the bubbles will be successfully delivered to the froth phase. Frothers stabilise bubbles by reducing the surface tension at the air–water interface. Frothers have a hydrophobic chain that is attracted to the air environment and a hydrophilic head that sits on the boundary in contact with water. Frothers also help to prevent bubble coalescence, maintaining a high

surface area for particle–bubble contact. In biobeneficiation, microorganisms have been reported to work as frothers [10][11][7][8][12][13].

Collectors increase the tendency of minerals to attach to bubbles. Like frothers, they are generally heteropolar, having a hydrophobic chain and a hydrophilic head. The hydrophilic head is attached to the mineral surface and the hydrophobic chains surround the mineral, rendering the mineral particles hydrophobic. Conventional chemical collectors find application here along with bio-depressants. However, some microorganisms, as will be discussed more deeply in the subsequent sections, have been reported to act as collectors [10][11][12][13].

There are three main classes of regulators: activators, depressants and pH modifiers. Regulators support the work of collectors by activating wanted minerals for collector adsorption, by passivating unwanted minerals against collector adsorption, or by ensuring that the pH is conducive to collector adsorption. Without regulators, the collectors may not be very effective. Most collectors are stable under alkaline conditions [14]. Microorganisms are generally employed to complement the action of synthetic collectors by preferentially suppressing unwanted species. However, it has been found that microorganisms may also serve as collectors, and could replace synthetic reagents [15].

Flotation plays a critical role as a concentration technique in PGM processing. The technique is a complex engineering process that requires careful control of parameters such as pH, temperature, agitation speed, particle size, reagent dosage, etc. Flotation of PGMs occurs at a pH of 9 and at 25 °C [16], and involves the addition of depressants, collectors and frothers. Examples of PGM depressants, frothers and collectors are carboxymethyl cellulose (CMC), methyl isobutyl carbinol (MIBC) and sodium isobutyl xanthate (SIBX), respectively. Careful optimisation of reagent dosages is required for effective flotation. In addition to reagent optimisation, particle size is another parameter that must be controlled. It can be deduced from **Figure 4** that there is an optimum particle size for flotation performance, and that an inverse relationship exists between recovery and grade.

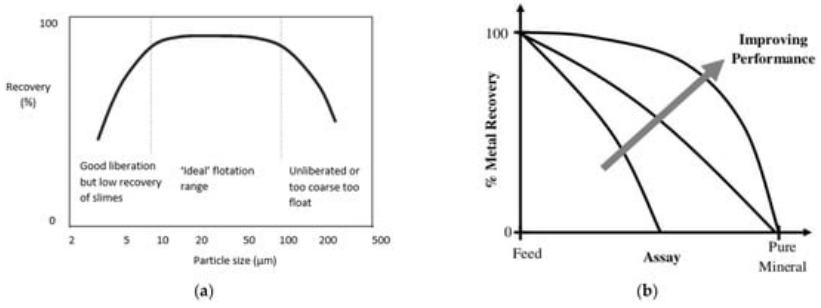

Figure 4. (**a**) Typical recovery–particle size curve, adapted from Pearse [17]; (**b**) typical recovery-grade curve, adapted from Klassen and Mokrousov [18].

Although considerable success has been achieved, sustainable froth flotation using chemical reagents is becoming more challenging [18]. High-grade ores are diminishing, and consequently gangue content is increasing [18]. Furthermore, mineral-bearing ores are becoming more complex [19]. Therefore, the amount of flotation reagents required for effective flotation is continually increasing. It has been reported [19] that to maintain efficient flotation operations as before, an annual 2–3% increase in the use of flotation reagents will be required. The cost attached to using flotation reagents will obviously increase, and the fact that flotation reagents are not recyclable implies that the technique is increasingly becoming unsustainable. Some flotation reagents pose a threat to the environment due to their toxicity. These challenges associated with flotation reagents have necessitated investigation of bio-reagents. Bio-reagents are cheaper to produce, less toxic, and biodegradable. The use of bacterially-generated reagents in flotation has been found to be effective, and it has been reported that bio-reagents may function, at least, as biocollectors, biodepressants and biofrothers [10][11][7][8][12][13]. The following sections will be focused on the microorganisms that have been found to be effective in the flotation of mineral species associated with PGMs.

2. Biobeneficiation of Base Metal Sulphides Associated with PGMs

Generally, PGMs are closely associated with BMS such that the recoveries of PGMs are closely related to those for the associated BMS. Therefore, work on the biorecovery of BMS can serve as an important guide for the biorecovery of PGMs. Bioflotation of BMS has been carried out using a number of microorganisms that may in turn be used for the recovery of PGMs. This section looks at the biobeneficiation (bioflotation and bioflocculation) of base metal sulphides using several microorganisms reported in previous studies. In terms of the base metal sulphides, the focus will be on those base metal sulphides closely associated with PGMs, i.e., chalcopyrite, pyrrhotite, pyrite and pentlandite.

2.1. Bacillus polymyxa

Pyrite has been removed by flotation and flocculation from quartz and calcite gangue minerals in the presence of bacterial cells and metabolic byproducts of *Bacillus polymyxa* [20]. The presence of microorganisms and their metabolic products alters the mineral surfaces, resulting in flotation or flocculation [21]. The bacterial cells and metabolic products of *Bacillus polymyxa* interact with the mineral species, resulting in changes of zeta potential and pH to conditions favorable for the flocculation and flotation of pyrite and chalcopyrite in the desulphurization of mine tailings [22]. In the removal of pyrite and chalcopyrite from oxide gangue minerals, the extracellular bacterial protein produced by *P. polymyxa* flocculated both chalcopyrite and pyrite, but resulted in the dispersion of quartz. Further separation of quartz from chalcopyrite was possible by flotation due to the increased hydrophobicity of quartz surfaces by bioprotein [22]. The bioprotein that induces hydrophobicity on mineral surfaces is secreted by bacteria [23]. Thus, *B. polymyxa* might be useful in the biobeneficiation of PGM minerals closely associated with pyrite and chalcopyrite. For effective flotation recovery, there is a need to use conventional xanthates after preconditioning with *B. polymyxa* cells.

2.2. Paenibacillus polymyxa

Separation of chalcopyrite from pyrite has also been achieved with the use of *Paenibacillus polymyxa* cells, which preferentially depressed pyrite [9]. Investigations were carried out using both adapted and unadapted cells. Adaptation was done by repeated culturing in the presence of chalcopyrite and pyrite. After exposure to *P. polymyxa* bacteria, both chalcopyrite and pyrite were then subjected to xanthate flotation. The reason for the selective depression of pyrite could not be fully established as there was bacterial adsorption on both pyrite and chalcopyrite [9], however, it was found that the surface potentials of the bacterial cells were different between the two mineral types. This was attributed to the different cell potentials and different amounts of proteins and polysaccharides present on the mineral surfaces. The depressing effect was greater for the adapted *P. polymyxa* than for the unadapted cells. Similar findings were observed in later work [24]. Thus, adapted *P. polymyxa* cells can be used to effectively depress pyrite. Furthermore, the presence of a xanthate (potassium isopropyl) after biodepression can enhance selectivity between chalcopyrite and pyrite [24].

2.3. Mycobacterium phlei

The highly hydrophobic bacteria *Mycobacterium phlei* was found to selectively attach to coal and not to pyrite [25]. The hydrophobicity so induced led in turn to clustering of coal particles, promoting flocculation. Similar results [26] have been reported for constituents of *M. phlei*; such as fatty acids were responsible for the hydrophobic interactions with coal particles. However, it was also found that although *M. phlei* selectively agglomerated coal, a significant portion of pyrite was entrapped in the coal agglomerates [27]. Subsequently, column flotation tests were done to further separate coal from contaminants such as pyrite [26]. The results from the studies with *M. phlei* in coal cleaning [27][25] can therefore be extrapolated for the concentration of PGMs associated with pyrite, knowing that this bacteria does not attach to pyrite and induces hydrophobicity in those particles it attaches to. Concentration of PGMs associated with pyrite using *M. phlei* may be possible by either flocculation or flotation, or by a combination of both techniques.

2.4. Acidithiobacillus ferrooxidans

Separation of chalcopyrite from pyrite under acidic and neutral conditions has been one of the greatest challenges in mineral beneficiation, as these minerals respond to xanthate collectors in a similar way. The addition of *Acidithiobacillus ferrooxidans* has been noted to promote the selective flotation of chalcopyrite under acidic and alkaline conditions, leaving behind pyrite [28]. The bacterium preferentially attaches to the pyrite surfaces, rendering the mineral hydrophilic [29][30]. The use of *A. ferrooxidans* reduced pyrite floatability by ~70%. Another study [31] observed depression of pyrite by *A. ferrooxidans*, leading to a 50% reduction in pyrite recovery.

In much earlier studies [32], an 80% reduction in pyrite floatability was reported. The results by Nagaoka et al. [29] were very interesting considering that *A. ferrooxidans* did not have the same depressing effect on minerals such as chalcocite, molybdenite, millerite and galena. It was also found that the recovery of chalcopyrite was not affected by *A. ferrooxidans* [31]. The preferential adhesion of *A. ferrooxidans* on pyrite over other sulphides was reported to be due to the presence aporusticyanin located on the surface of the bacterial cell [33]. However, an earlier study [34] proposed that the depression of pyrite by *A. ferrooxidans* was mainly due to the formation of hydrophilic jarosite on the pyrite surface, rendering pyrite unfloatable. According to Chandraprabha et al. [21], the depression of minerals is due to buildup of oxidized layers on mineral surfaces as a result of prolonged bacterial interaction. During prolonged bacterial interaction, the elemental S from bio-oxidation is re-oxidized to sulfoxy compounds, which in turn are oxidized to unfloatable sulphates. Some of the sulphates so formed will then dissolve and expose fresh minerals to bio-flotation.

Although the mechanism of pyrite depression by *A. ferrooxidans* is not very clear, with various contradicting theories, the depression of pyrite with *A. ferrooxidans* is indisputable. On the other hand, it has been indicated that *A. ferrooxidans* can also act as a promoter of flotation for some sulphide minerals due to oxidation and subsequent formation of elemental sulphur on the surfaces of minerals [35]. Therefore, it would be reasonable to propose the use of *A. ferrooxidans* in the flotation recovery of PGMs. *A. ferrooxidans* has great potential to either depress or float minerals associated with PGMs.

As mentioned earlier, *A. ferrooxidans* has been found to be more effective in the suppression of pyrite than NaCN [36]. The presence of *A. ferrooxidans* reduced pyrite recovery from 38.11% to 23.52% and promoted the grade of the target mineral. *A. ferrooxidans* can work along with a collector such as potassium isopropyl xanthate, provided a proper conditioning sequence is followed. However, the use of *A. ferrooxidans* results in less collector usage [37]. A conditioning time of 20 min was recommended for effective pyrite suppression [36]. The conditioning should be done in a medium containing soluble ferrous ions that are used as a growth substrate for *A. ferrooxidans* [38]. Simultaneous interaction of minerals with bacterial cells and collector was also recommended [28].

Similar results were also observed for the separation of pyrrhotite and chalcopyrite using *A. ferrooxidans* [39]. *A. ferrooxidans* preferentially attached to pyrrhotite, rendering the mineral hydrophilic such that only chalcopyrite was recovered in the froth phase. The increase in chalcopyrite floatability was due to the formation of elemental sulphur (S^0) due to bacterial activity. It was inferred that the hydrophobicity of chalcopyrite was increased by the S^0 [39], as well as due the reaction of Cu from the chalcopyrite with the xanthate molecules, as reported in previous work [40][41], because the reaction of Cu with xanthate molecules is more likely to have increased the hydrophobicity of chalcopyrite and enhanced the flotation process. Although the formation of S^0 would be expected to increase the floatability of pyrrhotite, this is counteracted by the high density of the hydrophilic cells created after microbe attachment [39]. Although contact angle values were not given [39], values of up to 80° are required for high hydrophobicities. **Figure 5** [39] shows the effects of *A. ferrooxidans* on chalcopyrite and pyrrhotite.

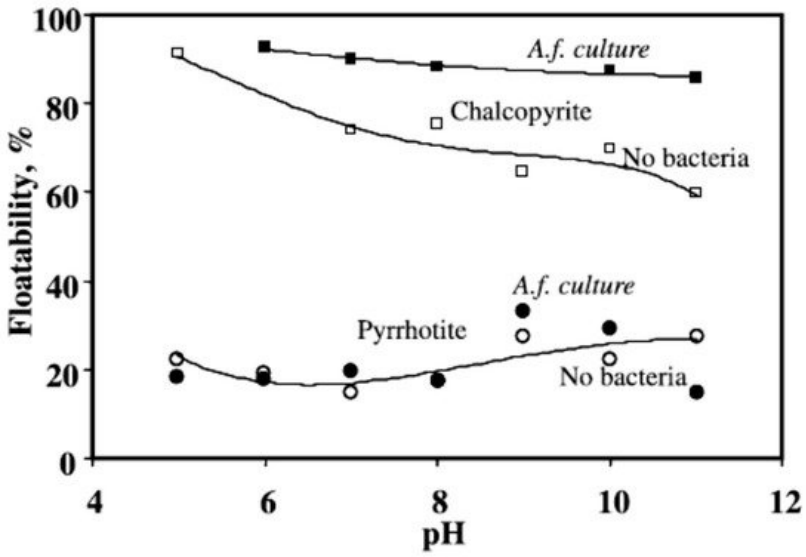

Figure 5. Floatability of chalcopyrite and pyrrhotite in the presence of a collector with (solid symbols) and without bio-modification (open symbols). Adapted from Pecina-Treviño et al. [39].

Although *A. ferrooxidans* is acidophilic, it has been proven that it can function as a pyrite depressant at higher pH (of ~8) values [42]. The increase in the depressing capability of *A. ferrooxidans* has been attributed to the increase of bacterial attachment density on pyrite [43]. In other words, although *A. ferrooxidans* loses its oxidative capacity at higher pH, it is still able to attach to pyrite surfaces and cause biodepression. Thus, it might not be necessary to add any acids during the conditioning stage, as *A. ferrooxidans* can function as a depressant under alkaline conditions. The collector efficiency, however, can be compromised when *A. ferrooxidans* is used in sea water [43]. It was found that the addition of *A. ferrooxidans* to sea water resulted in an increased pyrite contact angle with the collector. The modification of the mineral surface by bacteria may have caused decreased influence of the collector on pyrite than when only sea water was used for conditioning. Although not investigated, collector efficiency must have also been compromised in previous work that was done under similar conditions [42]. Thus, *A. ferrooxidans* suppresses pyrite by inhibiting collector action as a result of increased bacterial density on the pyrite surface.

The depression of pyrite by *A. ferrooxidans* under mildly alkaline conditions (pH of 8) has also been observed [44]. The pH for pyrite depression is close to that reported for PGM flotation, i.e., a pH of 9 [45]. Although pyrite depression occurred under alkaline conditions, prior surface modification by bacteria was done at a pH of 2, conducive to bacterial activity. It

was also found that for effective biodepression of pyrite, considerable time was required for conditioning and to adapt the bacterial culture [44]. The adapted culture would then be separated from pyrite slurries by filtration and used for bioconditioning of pyrite flotation slurries.

In another study [46], the use of extracellular polymeric substances (EPS) produced during the early stage of *A. ferrooxidans* attachment to minerals was recommended for effective pyrite suppression. EPS are bacterial metabolites that surround the cells and assist with bacterial attachment to mineral surfaces [42]. Production of EPS is not a function of pH [42], which plays a contributing role to biodepression by *A. ferrooxidans* even under alkaline conditions. *A. ferrooxidans* has also been reported to be effective in the flocculation of both pyrite and chalcopyrite, separating them from non-sulphide minerals [38].

2.5. Acidithiobacillus thiooxidans

Separation of pyrite and chalcopyrite has been done using *Acidithiobacillus thiooxidans* [6][36]. It was possible to separate chalcopyrite from pyrite under both acidic and neutral conditions [6]. Thus, like *A. ferrooxidans*, *A. thiooxidans* preferentially suppresses pyrite, resulting in flotation of chalcopyrite. The survival of *A. thiooxidans* is aided by the formation of biofilms [47]. However, *A. thiooxidans* (and *A. ferrooxidans*), if not adapted, do not thrive well in the presence of Cu ions at high concentrations [39][6][48], which explains why they adsorb less on chalcopyrite. After the depression of pyrite, the flotation of chalcopyrite can be carried out using conventional reagents. In cases where chalcopyrite has to be depressed by the same bacteria and recovered by reverse flotation, the bacteria would have to be firstly adapted to Cu ions.

2.6. Leptospirillum ferrooxidans

Leptospirillum ferrooxidans has been reported to be useful in the separation of pyrite and chalcopyrite [37]. *L. ferrooxidans* has been observed to preferentially depress chalcopyrite, as it adsorbs more on chalcopyrite than on pyrite. The preferential depression of chalcopyrite is due to higher cell adsorption density [37]. Because the surface area of chalcopyrite is twice that of pyrite, the higher cell adsorption of *L. ferrooxidans* on chalcopyrite than on pyrite has been attributed to chalcopyrite having more surface defects, promoting access to the energy source (Fe) by the bacteria [37]. However, opposite results were found in later work which showed that *L. ferrooxidans* selectively attached more on pyrite than on chalcopyrite, leading to the recovery of chalcopyrite. This work, however, indicated that the growth conditions of the *L. ferrooxidans* influence the outcome of flotation results, and that under certain conditions it might be possible to depress chalcopyrite as well. A modified *Leptospirillum* HH was used for growing *L. ferrooxidans* [37]. On the other hand, the best separation was obtained when *L. ferrooxidans* grew on chalcopyrite [49]. The contradictory flotation results between the different studies [37][49] might be due to their different methods of growing *L. ferrooxidans*.

Extracellular polymeric substances (EPS) derived from *L. ferrooxidans* were found to be more effective than the *L. ferrooxidans* cultures [49]. Thus, improved chalcopyrite recovery and greater depression of pyrite was achieved with the use of EPS extracted from *L. ferrooxidans*. The EPS were produced by growing *L. ferrooxidans* on chalcopyrite. It was also found that EPS have better attachment at the mineral surfaces than their parent microorganisms thanks to their higher concentrations of polysaccharides [42][50][51].

The recovery of chalcopyrite in the presence of *L. ferrooxidans* has been reported by Diaz-Lopez et al. [52]. They, however, found that the recovery of chalcopyrite decreased in the presence of pyrrhotite [52]. The presence of pyrrhotite results in galvanic interactions with chalcopyrite [52]. These galvanic interactions cause anodic reactions on chalcopyrite surfaces, rendering a degree of hydrophilicity and, consequently, a decrease in chalcopyrite recovery. Some of the pyrrhotite is also recovered in the froth phase because the depressing effect of *L. ferrooxidans* is countered by the oxidation of pyrrhotite arising from galvanic interaction with chalcopyrite [52]. In another study [53] contrary results were obtained, with the flotation recovery of chalcopyrite increasing in the presence of *L. ferrooxidans* due to the formation of hydrophobic species. It therefore appears that the depressive effect of *L. ferrooxidans* depends on the xanthate concentration. Certain xanthate dosages result in the counter-creation of species on the chalcopyrite surfaces, resulting in good flotation recoveries. Thus, it is important to optimize the dosage of reagents, as remarked upon in [36].

2.7. Bacillus subtilis

Bacillus subtilis was found to have a depressing effect on pyrite [54]. The microorganisms had a high affinity for the pyrite surfaces, rendering them hydrophilic. Unlike the previously-reported microorganisms, efficient flotation of galena from pyrite was achieved in the absence of a conventional collector. According to Sarvamangala et al. [54], pyrite was suppressed by the exopolysaccharides that were produced, whereas galena surfaces were rendered hydrophobic by the extracellular proteins that were generated. *Bacillus subtilis* was effective as a flocculant for pyrite as well [54].

2.8. Bacillus pumilus and Alicyclobacillus ferrooxidans

Bacillus pumilus and *Alicyclobacillus ferrooxidans* have been found to act as both collectors and depressants for pyrite [15]. The biosurfactants created by these bacteria form contact angles with pyrite surfaces that decrease with time of incubation. The decrease in contact angles leads to transformation from hydrophobic surfaces (collectors) to hydrophilic surfaces (depressants). This dual function of *Bacillus pumilus* and *Alicyclobacillus* makes them different from the other types of biosurfactant-forming microorganisms.

2.9. Halophilic Bacteria

Halophilic bacteria have been successfully used as a substitute for lime as a depressant of pyrite, promoting the selective flotation of chalcopyrite [55]. However, the attachment mechanism of halophilic bacteria to pyrite is not yet clear, although it appears to be of a hydrophobic nature. The relevant studies were conducted in sea water at a pH of ~8 [42].

2.10. Sulphate-Reducing Bacteria

Sulphate-reducing bacteria (SRB) of the type *Desulfovibrio* have also been reported to be useful in the biobeneficiation of minerals, having a depressing effect on chalcopyrite [35]. The main advantage of SRB is that process conditions can be controlled such that the bacteria may either generate a sulphide product that promotes flotation or the H_2S depressant, depending on the mineral of interest.

2.11. Mixed Cultures

Most biobeneficiation work has been based on pure cultures. The use of mixed bioleaching cultures of heterotrophic and chemolithotrophic bacteria and their EPS in chalcopyrite flotation was investigated by Govender and Gericke [56]. It was demonstrated that free EPS derived from mixed bioleaching microbes was a potential flotation agent for sulphide minerals. The use of EPS extracted from mixed bioleaching cultures resulted in selective flotation of chalcopyrite from pyrite, and chalcopyrite recoveries of ~70% were attained. It was noted that the use of EPS extracted from mixed bioleaching cultures might improve the flotation of chalcopyrite.

2.12. Biobeneficiation of Pentlandite

Although no information has been found regarding biobeneficiation of pentlandite, postulations can be made based on other minerals. For example, the preferential suppression by *A. ferrooxidans* of pyrite over non-ferrous galena due to the formation of hydrophilic jarosite [21] implies that because ferrous pentlandite is likely to form jarosite, it can consequently be depressed by *A. ferrooxidans*.

In terms of flocculation, it has also been reported that only sulphide minerals (pyrite and chalcopyrite) were flocculated by *A. ferrooxidans*, leaving behind only the non-sulphide species [38]. Thus, it is likely that sulphide-bearing pentlandite would be flocculated by use of *A. ferrooxidans*. Furthermore, it has been reported that any sulphide mineral can be floated if the correct pH can be established [35]. Therefore, as long as the correct pH is established, flocculation of pentlandite should be possible.

The sulphate-reducing bacteria have been reported to have a dual effect on chalcopyrite, acting as a depressant or promoting flotation [35]. The dual role for the SRB has been noted to be as a result of the manipulation of the process conditions to either generate a sulphide product or H_2S depressant. It is highly likely that the same reactions can be produced with pentlandite (S-bearing), thus allowing biobeneficiation with SRB.

It is likely that the free EPS derived from mixed bioleaching microbes that were able to separate chalcopyrite and pyrite [56] could also be used for the biobeneficiation of pentlandite. However, it cannot be postulated whether these would promote flotation or act as a depressant.

References

1. Crabtree, E.H.; Vincent, J.D. The early days of froth flotation. In Froth Flotation—50th Anniversary; AIMME: New York, NY, USA, 1962; pp. 39–54.
2. Engelbrecht, J. Potential Changes in the Physical Beneficiation Processes That Can Improve the Recovery Grade or Costs for the Platinum Group Metals. In Proceedings of the Fifth International Platinum Conference: A Catalyst for Change, Sun City, South Africa, 18–20 September 2012.

3. Junge, M.; Oberthür, T.; Kraemer, D.; Melcher, F.; Piña, R.; Derrey, I.T.; Manyeruke, T.; Strauss, H. Distribution of platinum-group elements in pristine and near-surface oxidized Platreef ore and the variation along strike, northern Bushveld Complex, South Africa. Miner. Depos. 2019, 54, 885–912.
4. Filippov, L.O.; Filippova, I.V.; Severov, V.V. The use of collectors mixture in the reverse cationic flotation of magnetite ore: The role of Fe-bearing silicates. Miner. Eng. 2010, 23, 91–98.
5. Wark, I.W.; Cox, A.B. Principles of flotation, III. Trans. AIME 1934, 112, 267–301.
6. Chandraprabha, M.N.; Natarajan, K.A. Surface chemical and flotation behaviour of chalcopyrite and pyrite in the presence of Acidithiobacillus thiooxidans. Hydrometallurgy 2006, 83, 146–152.
7. Deo, N.; Natarajan, K.A. Interaction of Bacillus polymyxa with some oxide minerals with reference to mineral beneficiation and environmental control. Miner. Eng. 1997, 10, 1339–1354.
8. Patra, P.; Natarajan, K.A. Role of mineral specific bacterial proteins in selective flocculation and flotation. Int. J. Miner. Process. 2008, 88, 53–58.
9. Sharma, P.K.; Rao, K.H. Role of a heterotrophic Paenibacillus polymyxa bacteria in the bioflotation of some sulfide minerals. Mining Metall. Explor. 1999, 16, 35–41.
10. Hosseini, T.R.; Kolahdoozan, M.; Tabatabaei, Y.S.M.; Oliazadeh, M.; Noaparast, M.; Eslami, A.F.S.A.R.; Manafi, Z.; Alfantazi, A. Bioflotation of Sarcheshmeh copper ore using Thiobacillus ferrooxidans bacteria. Miner. Eng. 2005, 18, 371–374.
11. Botero, A.E.C.; Torem, M.L.; de Mesquita, L.M.S. Fundamental studies of Rhodococcus opacus as a biocollector of calcite and magnesite. Miner. Eng. 2007, 20, 1026–1032.
12. Vasanthakumar, B.; Ravishankar, H.; Subramanian, S. A novel property of DNA—As a bioflotation reagent in mineral processing. PLoS ONE 2012, 7, e39316.
13. Behera, S.K.; Mulaba-Bafubiandi, A.F. Microbes assisted mineral flotation a future prospective for mineral processing industries: A review. Miner. Process. Extr. 2017, 38, 96–105.
14. Wills, B.A.; Naier-Munn, T. Froth Flotation. In Mineral Processing Technology: An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, 7th ed.; Elsevier Science and Technology Books: Amsterdam, The Netherlands, 2013; pp. 267–352.
15. Sanwani, E.; Chaerun, S.; Mirahati, R.; Wahyuningsih, T. Bioflotation: Bacteria-mineral interaction for eco-friendly and sustainable mineral processing. Procedia Chem. 2016, 19, 666–672.
16. Sheni, N.; Corin, K.; Wiese, J. Considering the effect of pulp chemistry during flotation on froth stability. Miner. Eng. 2018, 116, 15–23.
17. Pearse, M.J. An overview of the use of chemical reagents in mineral processing. Miner. Eng. 2005, 18, 139–149.
18. Klassen, V.I.; Mokrousov, V.A. An Introduction to the Theory of Flotation; Butterworth: Oxford, UK, 1963.
19. Bulatovic, S.M. Handbook of Flotation Reagents: Chemistry, Theory and Practice: Volume 1: Flotation of Sulfide Ores; Elsevier: Amsterdam, The Netherlands, 2007.
20. Patra, P.; Natarajan, K.A. Microbially-induced flocculation and flotation for pyrite separation from oxide gangue minerals. Miner. Eng. 2003, 16, 965–973.
21. Chandraprabha, M.N.; Natarajan, K.A. Microbially induced mineral beneficiation. Miner. Process. Extr. 2009, 31, 1–29.
22. Patra, P.; Natarajan, K.A. Microbially enhanced removal of pyrite and chalcopyrite from oxide gangue minerals with reference to desulfurization of tailings. Mining Metall. Explor. 2004, 21, 169–178.
23. Santhiya, D.; Subramanian, S.; Natarajan, K.A. Surface chemical studies on sphalerite and galena using extracellular polysaccharides isolated from Bacillus polymyxa. J. Colloid Interface Sci. 2002, 256, 237–248.
24. Sharma, P.K.; Rao, K.H. Adhesion of Paenibacillus polymyxa on chalcopyrite and pyrite: Surface thermodynamics and extended DLVO theory. Colloids Surf. B Biointerfaces 2003, 29, 21–38.
25. Misra, M.; Smith, R.W.; Dubel, J.; Chen, S. Selective flocculation of fine coal with hydrophobic Mycobacterium phlei. Mining Metall. Explor. 1993, 10, 20–23.
26. Raichur, A.M.; Misra, M.; Smith, R.W. Differential adhesion of hydrophobic bacteria onto coal and associated minerals. Coal Prep. 1995, 16, 51–63.
27. Raichur, A.M.; Misra, M.; Bukka, K.; Smith, R.W. Flocculation and flotation of coal by adhesion of hydrophobic Mycobacterium phlei. Colloids Surf. B Biointerfaces 1996, 8, 13–24.

28. Chandraprabha, M.N.; Natarajan, K.A.; Modak, J.M. Selective separation of pyrite and chalcopyrite by biomodulation. Colloids Surf. B Biointerfaces 2004, 37, 93–100.

29. Nagaoka, T.; Ohmura, N.; Saiki, H. A novel mineral flotation process using Thiobacillus ferrooxidans. Appl. Environ. 1999, 65, 3588–3593.

30. Dwyer, R.; Bruckard, W.J.; Rea, S.; Holmes, R.J. Bioflotation and bioflocculation review: Microorganisms relevant for mineral beneficiation. Miner. Process. Extr. 2012, 121, 65–71.

31. Kolahdoozan, M.; Tabatabaei Yazdi, S.M.; Yen, W.T.; Hosseini Tabatabaei, R.; Shahverdi, A.R.; Oliazadeh, M.; Noaparast, M.; Eslami, A.; Manafi, Z. Bioflotation of the low grade Sarcheshmeh copper sulfide. Trans. Indian Inst. Met. 2004, 57, 485–490.

32. Atkins, A.S.; Bridgwood, E.W.; Davis, A.J.; Pooley, F.D. A study of the suppression of pyritic sulphur in coal froth flotation by Thiobacillus ferrooxidans. Coal Prep. 1987, 5, 1–13.

33. Blake II, R.C.; Sasaki, K.; Ohmura, N. Does aporusticyanin mediate the adhesion of Thiobacillus ferrooxidans to pyrite? Hydrometallurgy 2001, 59, 357–372.

34. Misra, M.; Chen, S. The effect of growth medium of Thiobacillus ferrooxidans on pyrite and galena flotation. Miner. Eng. 1996, 9, 157–168.

35. Natrajan, K.A. Biotechnology for metal extraction, mineral beneficiation and environmental control. In Proceedings of the International Seminar on Mineral Processing Technology and Indo-Korean Workshop on Resource Recycling (MPT-2006), Chennai, India, 8–10 March 2006; Volume 1, pp. 68–81.

36. Mehrabani, J.V.; Noaparast, M.; Mousavi, S.M.; Dehghan, R.; Rasooli, E.; Hajizadeh, H. Depression of pyrite in the flotation of high pyrite low-grade lead–zinc ore using Acidithiobacillus ferrooxidans. Miner. Eng. 2010, 23, 10–16.

37. Vilinska, A.; Rao, K.H. Leptosririllum ferrooxidans-sulfide mineral interactions with reference to bioflotation and bioflocculation. Trans. Nonferrous Met. Soc. China 2008, 18, 1403–1409.

38. Natarajan, K.A.; Das, A. Surface chemical studies on ‘Acidithiobacillus’ group of bacteria with reference to mineral flocculation. Int. J. Miner. Process 2003, 72, 189–198.

39. Pecina-Treviño, E.T.; Ramos-Escobedo, G.T.; Gallegos-Acevedo, P.M.; López-Saucedo, F.J.; Orrantia-Borunda, E. Bioflotation of sulfide minerals with Acidithiobacillus ferrooxidans in relation to copper activation and surface oxidation. Can. J. Microbiol. 2012, 58, 1073–1083.

40. Abramov, A.; Avdohin, V.M. Oxidation of Sulfide Minerals in Benefication Processes; Gordon and Breach Science Publishers: Amsterdam, The Netherlands, 1998.

41. Leja, J. Collector Mechanism, I. Thiol collectors in sulfide minerals. In Surface Chemistry of Froth Flotation, 2nd ed.; Rao, S.R., Ed.; Springer: Boston, MA, USA, 2004; Volume 1, pp. 479–526.

42. San Martín, F.; Kracht, W.; Vargas, T. Biodepression of pyrite using Acidithiobacillus ferrooxidans in seawater. Miner. Eng. 2018, 117, 127–131.

43. San Martín, F.; Kracht, W.; Vargas, T.; Rudolph, M. Mechanisms of pyrite biodepression with Acidithiobacillus ferrooxidans in seawater flotation. Miner. Eng. 2020, 145, 106067.

44. Attia, Y.A.; Elzeky, M.; Ismail, M. Enhanced separation of pyrite from oxidized coal by froth flotation using biosurface modification. Int. J. Miner. Process. 1993, 37, 61–71.

45. Muzenda, E.; Afolabi, A.S.; Abdulkareem, A.S.; Ntuli, F. Effect of pH on the Recovery and grade of base metal sulphides (PGMs) by flotation. In Proceedings of the World Congress on Engineering and Computer Science, San Francisco, CA, USA, 19–21 October 2011; Volume 2, p. 2.

46. La Vars, S.M.; Newton, K.; Quinton, J.S.; Cheng, P.Y.; Wei, D.H.; Chan, Y.L.; Harmer, S.L. Surface chemical characterisation of pyrite exposed to Acidithiobacillus ferrooxidans and associated extracellular polymeric substances. Minerals 2018, 8, 132.

47. Jefferson, K.K. What drives bacteria to produce a biofilm? FEMS Microbiol. Lett. 2004, 236, 163–173.

48. Das, A.; Modak, J.M.; Natarajan, K.A. Surface chemical studies of Thiobacillus ferrooxidans with reference to copper tolerance. Antonie Van Leeuwenhoek 1998, 73, 215–222.

49. Bleeze, B.; Zhao, J.; Harmer, S.L. Selective attachment of Leptospirillum ferrooxidans for separation of chalcopyrite and pyrite through bio-flotation. Minerals 2018, 8, 86.

50. Harneit, K.; Göksel, A.; Kock, D.; Klock, J.H.; Gehrke, T.; Sand, W. Adhesion to metal sulfide surfaces by cells of Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans and Leptospirillum ferrooxidans. Hydrometallurgy 2006, 83, 245–254.

51. He, Z.G.; Yang, Y.P.; Shan, Z.H.O.U.; Hu, Y.H.; Zhong, H. Effect of pyrite, elemental sulfur and ferrous ions on EPS production by metal sulfide bioleaching microbes. Trans. Nonferrous Met. Soc. China 2014, 24, 1171–1178.
52. Díaz-López, C.V.; Pecina-Treviño, E.T.; Orrantia-Borunda, E. A study of bioflotation of chalcopyrite and pyrrhotite mixtures in presence of L. ferrooxidans. Can. Metall. Quart. 2012, 51, 118–125.
53. Pecina, E.T.; Rodriguez, M.; Castillo, P.; Diaz, V.; Orrantia, E. Effect of Leptospirillum ferrooxidans on the flotation kinetics of sulphide ores. Miner. Eng. 2009, 22, 462–468.
54. Sarvamangala, H.; Natarajan, K.A.; Girisha, S.T. Microbially-induced pyrite removal from galena using Bacillus subtilis. Int. J. Miner. Process 2013, 120, 15–21.
55. Consuegra, G.L.; Kutschke, S.; Rudolph, M.; Pollmann, K. Halophilic bacteria as potential pyrite bio-depressants in Cu-Mo bioflotation. Miner. Eng. 2020, 145, 106062.
56. Govender, Y.; Gericke, M. Extracellular polymeric substances (EPS) from bioleaching systems and its application in bioflotation. Miner. Eng. 2011, 24, 1122–1127.