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Review

Towards the Biobeneficiation of PGMs: Reviewing the Opportunities

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Abstract: 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. In conventional flotation, the flotation behavior of the associated sulphides determines overall PGM recovery. The same principle may also be applied for the bio-beneficiation of PGMs. Therefore, this paper discusses the biobeneficiation behavior of sulphides closely associated with PGMs with the aim of postulating the bio-beneficiation behavior of PGMs associated with the same base metal sulphides. Conventional PGM processes are briefly discussed, as bio-beneficiation of PGMs is governed by similar underlying principles. Potential microorganisms for the biobeneficiation of PGMs are highlighted, as well as the corresponding conditions for their effectiveness. The use of both single cultures and mixed cultures is discussed. Depending on conditions, PGMs associated with pyrite and/or chalcopyrite were projected to be biofloatable with *B. polymyxa*, *P. polymyxa*, *A. ferrooxidans*, *L. ferrooxidans*, *B. pumilus*, *B. subtilis*, halophilic bacteria, *Alicyclobacillus ferrooxidans*, sulphate reducing bacteria, and mixed cultures of *A. ferrooxidans*, *A. thiooxidans* and *L. ferrooxidans*. Pyrite-associated PGMsare expected to be generally prone to biodepression, whereas chalcopyrite-associated PGMs are expected to be generally recovered as the floatable phase. Sulphate-reducing bacteria were reported to have a dual role on the bioflotation of sulphide ores (flotation and depression), depending on the conditions. Therefore, this type of microorganism may serve as both a depressant or a collector in the recovery of PGMs. Based on the bioflotation response of pyrrhotite to *L. ferrooxidans*, it is anticipated that pyrrhotite-associated PGMS can be biodepressed using *L. ferrooxidans*. In terms of bioflocculation, PGMs associated with chalcopyrite may be recovered using *L. ferrooxidans*, whereas *A. ferrooxidans*, *A. thiooxidans*, *B. polyxyma* and *B. subtilis* can be used in the bioflocculation of pyrite-associated PGMs. *M. phlei* can be employed in the reverse bioflocculation of pyrite-associated PGMs. Although no information was found on the biobeneficiation of pentlandite, postulations were made based on other sulphide minerals. It was postulated that biobeneficiation (biodepression and bioflotation) with pentlandite-associated PGMs should be possible using *A. ferrooxidans*. It is also projected that sulphate-reducing bacteria will be suitable for the bioflotation of PGMs associated with pentlandite. The removal of gangue species such as silicates and chromites associated with PGM concentrates was also discussed. *A. ferrooxidans*, *P. polymyxa* and *B. mucilaginous* are candidates for the removal of gangue species. Furthermore, the need to control process conditions was highlighted. The most suitable conditions for biobeneficiation of the various base metal sulphide minerals associated with PGMs are presented in the paper. Most of the challenges associated with biobeneficiation of PGMs are already common to conventional methods, and the means of circumventing them are already well established. Developments in genetic engineering and the advent of new data science techniques are tools that could make the biobeneficiation of PGMs a possibility.

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1. Introduction

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 [1], flotation, and flocculation [2]. It is well known that both dead and living microorganisms as well as their products can act as flotation and flocculating agents by biomodification [3]. Several mechanisms have been proposed to explain biomodification of minerals. Biomodification may occur due to attachment of microbial cells to mineral surfaces [4–6]. It has been reported that oxidation reactions are responsible for bio-modification [7]. Another proposed mechanism for biomodification is the adsorption of bacterial proteins and exopolysaccharides on mineral surfaces and/or the chemical reaction of mineral surfaces with metabolite products [8]. The extent of bacterial adhesion onto a mineral surface depends on the mineral's chemical composition as well as on the dissolution and toxicity of the mineral substrate [9]. Bacterial surfaces generally have hydrophilic characteristics [5,10,11]; therefore, when bacteria adsorb onto mineral surfaces, they induce hydrophilicity and cause the mineral surfaces to be depressed in the flotation environment. However, there are cases where bacteria can cause either hydrophilicity or hydrophobicity, e.g., *Bacillus pumilus* and *Alicyclobacillus ferrooxidans* [12]. Such bacteria can therefore be used either as depressants or as collectors. Work has been published on the use of microorganisms as collectors, depressants and frothers in the flotation of minerals [5,6,13–16].

Biobeneficiation has been applied to such mineral ores as coal, iron, lead–zinc [17] and copper ores [9]. Increased floatability of the copper-bearing mineral chalcopyrite was found after adding a culture of *A. ferrooxidans* [9]. The same study [9] reported that for the flotation of copper ores, *A. ferrooxidans* can also work as a depressant, with potassium isopropyl xanthate being the collector. In two other separate studies [11,18], the grade of the final copper concentrate was increased when *A ferrooxidans* was employed. The presence of *A. ferrooxidans* promoted selective bio-oxidation and subsequent depression of pyrite. The ability of *A. ferrooxidans* to function as a pyrite depressant was also confirmed using the bacteria as a depressant in the flotation of zinc and lead concentrates instead of NaCN [17].

The beneficiation of iron ores by removing silica and alumina was reported to be possible with the use of *Paenibacillus polymyxa* [8]. On the other hand, flotation and flocculation of coal was reported to be enhanced by *Mycobacterium phlei* [19]. Similar results were also observed in the use of *A. ferrooxidans* [4]. It is worthwhile at this juncture to note that the microorganisms for biobeneficiation are also the same as those that are generally involved in bioleaching of the same minerals. Microorganisms adhere to mineral surfaces, resulting in surface modification and, subsequently, leaching reactions. However, oxidation/leaching reactions require a much longer time (several hours to several days), while bio-surface modification requires a much shorter time (a few minutes to less than an hour) [4]. Therefore, the difference in time between bio-surface modification and bio-oxidation/bioleaching makes it possible to use microorganisms for biobeneficiation without any bioleaching taking place. Furthermore, biobeneficiation can be done at temperatures as low as 30 °C [4], and at these temperatures, the kinetics for bioleaching are low [20].

Biobeneficiation of PGMs has not been explicitly reported; however, information on the behavior of minerals associated with PGMs is useful in predicting the biobeneficiation of PGMs. This logic is derived from conventional PGM flotation, where it is known that the flotation behavior of the associated sulphides determines overall PGM recovery [21,22]. For example, the recovery of pyrrhotite ($Fe_{1-x}S$), the main sulphide mineral in the Merensky ores, greatly influences the overall recovery of PGMs due to their contact with pyrrhotite [22]. The conventional surfactants attach to mineral surfaces chemically or physically,

whereas microorganisms attach by surface–surface interactions [23]. However, both processes involve the modification of mineral surfaces. It has also been found that unlike with conventional flotation reagents, fluid flow during flotation affects bacterial attachment, and is therefore worth considering during mineral–bacteria mixing [23]. This means that for bioprocessing, control of bacterial concentration might be more demanding than in conventional flotation. Thus, as in conventional beneficiation, knowledge of the flotation and flocculation behavior of various PGM-associated sulphide species in the presence of microorganisms is useful in the postulation of PGM biobeneficiation. Recovery of mineral species by flotation can be done as a direct process (where the mineral of interest is selected) or as a reverse process (where the gangue species are selected). Thus, information for both the selection and non-selection of PGM-associated minerals might be useful for PGM recovery.

It is anticipated that the introduction of microorganisms for PGM flotation might result in comparable PGM grades and recovery to that obtained using inorganic reagents. Comparable results were observed between *A. ferrooxidans*, *A thiooxidans* and NaCN as pyrite depressants [17]. Furthermore, the ability to culture and grow microorganisms means that they are economical in their application. Because most organisms are already part of the natural ecosystem, their use in flotation would be more environmentally friendly.

The aim of this paper is to provide the necessary knowledge for the biobeneficiation of PGMs from ores. This paper looks into the use of microorganisms in the physicochemical separation and coagulation of minerals (bioflotation and bioflocculation). As flotation is the most widely-used mineral concentration technique, this paper leans more on bioflotation than on bioflocculation. The next section provides a background on the typical chemical and mineralogical compositions of PGM ores as well as their mineral associations. This information is important, as mineralogy plays a critical role in mineral beneficiation. Conventional flotation is discussed in another section, as the principles thereof are key to the understanding of bioflotation as an alternative technology. The rest of the paper is then be devoted to discussing the biobeneficiation of various PGM-associated phases using different microorganisms. Finally, the challenges and opportunities of PGM bioprocessing are highlighted.

2. Chemical and Mineralogical Composition of PGMs and Their Mineral Associations

The largest deposit of PGMs in the world is the Bushveld complex in South Africa. The typical chemical compositions of PGM ores from the Bushveld complex of South Africa are shown in Table 1 [24]. As can be deduced from Table 1, the ores vary in composition, and consequently different concentrates are produced from these ores after flotation [24]. The concentrates produced vary in such aspects as overall PGM content, Pt/Pd ratio, base metal content, and Cr_2O_3 spinel content. As such, blending of the ores is often a necessity for optimum beneficiation. The typical mineralogical compositions and mineralisations of Bushveld complex PGM ores are shown in Tables 2–4 [25].

Generally, PGMs are associated with either chromitites or sulphide-rich rocks [26,27]. In chromite environments, PGEs occur in alloys, sulphides, arsenides, and sulpharsernides [28–30]. Bismuthotellurides are generally found in base metal sulphide systems such as the Merensky Reef, the Great Dyke and the Platreef [31–35]. PGE sulphides and arsenides are also found in base metal sulphide systems [36]; however, most PGMs occur as sulphides [37,38]. The PGMs exist within base metal sulphide (BMS) minerals or at the base metal–silicate grain boundary; as such, milled PGM ores can be floated to recover PGMs [36]. Generally, PGMs are associated with the BMS [39]. The main BMS associated with PGMs are shown in Table 3. Virgin ores consist mainly of pyrrhotite ($Fe_{1-x}S$) (~75%), pentlandite ($(Fe, Ni)_9S_8$), chalcopyrite ($CuFeS_2$), and minor quantities of pyrite (FeS_2) [36] It is against this background that this paper focuses on the biobeneficiation of pyrrhotite, pentlandite, chalcopyrite and pyrite. As there is strong link between the recovery of PGM-associated base metals and that of PGMs, information on the biobeneficiation of these base metals is of great importance in predicting PGM biobeneficiation.

Table 1. PGM assays from different sources, with normalised analysis of the four precious elements (4E) and of Ir and Ru with respect to the 6E [24].

Assay	Merensky	UG2	Platreef	Hi-Ni Platreef
PGM-4E	200	200	120	30
Pt-% of 4E	63.5	56.7	45.1	24.0
Pd	28.1	29.4	45.7	69.3
Rh	4.4	13.0	3.2	1.3
Au	4.0	0.9	6.0	5.4
Ir-% of 6E	0.6	1.6	1.0	-
Ru	6.8	9.6	3.5	-
Base metals (%)				
Ni	6.0	1.4	4.9	6.0
Cu	3.4	0.7	2.5	4.0
Co	0.15	0.05	0.2	0.07
Cr_2O_3 (%)	0.6	3.0	0.3	0.1
S (%)	15–20	4–6	10–15	15–20

Table 2. Typical bulk mineral compositions of the Merensky, UG2 and Platreef [25].

Mineral Name	Merensky Reef	UG2 Reef	Platreef
		Vol (%)	
Pyroxene	55–60	15–30	30–40
Feldspar	30–40	3–9	18
Chromite	6	50–75	-
Talc	<1	<1	<1
Serpentine	2–3	1	5
Amphibole	1–2	<1	4
Chlorite	1–2	<1	4
Mica	<1	<1	1
BMS	<1	<1	2
Other	1–2	<1	5

Table 3. Mineralisation of the Merensky, UG2 and Platreef ores with respect to base metal sulphides [25].

Minerals	Merensky Reef	UG2 Reef	Platreef
		Vol (%)	
Pentlandite	35	44–52	27
Pyrrhotite	46	26–35	52
Chalcopyrite	20	21	19

Table 4. PGM Mineralisation of the Merensky, UG2 and Platreef Ores [25].

Class	Minerals	Merensky Reef	UG2 Reef	Platreef
			Vol (%)	
PGM Alloys	Ferro platinum Pt Alloy Pd Alloy	40	40	11–30
	Electrum (Au)	2	0.2	3
Arsenides	Pt-arsenides Pd-arsenides	4	0.1–1	1–20
	PGE-sulphur arsenides	3	0.8–7	16–35
PGM sulphides	PtPd-sulphide Pt-sulphide PtRh-sulphide	16	40–60	1–7
Tellurides	Pt-tellurides Pd-tellurides	35	0.5–5	20–50

3. 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 [40]. 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.

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

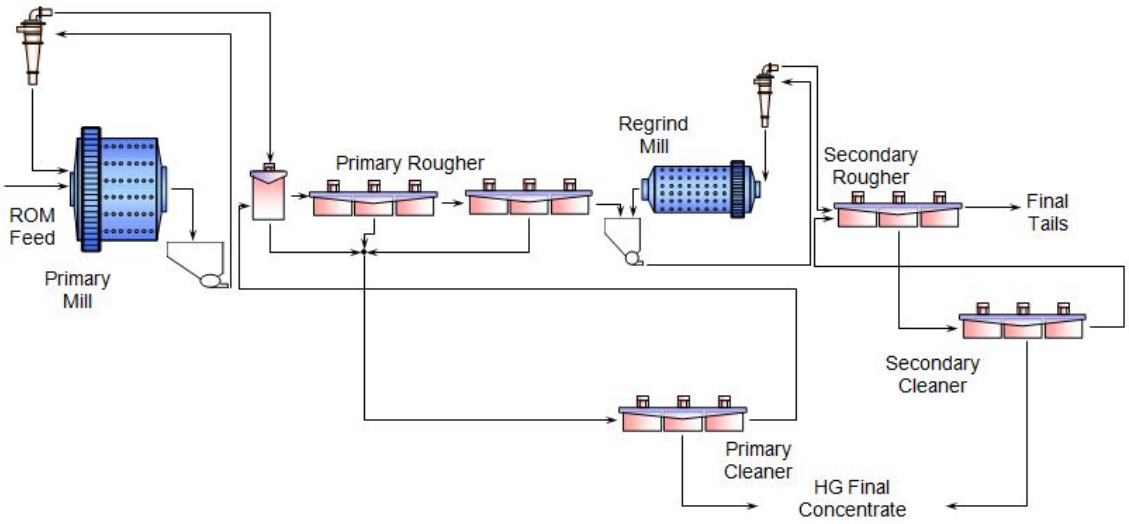

Figure 1. Typical concentration plant for the processing of PGMs, adapted from Engelbrecht [41].

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 poten-

tials on mineral particles, while the opposite is true under acidic conditions. A typical relationship between pH and zeta potential is shown in Figure 2 [42]. 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 [43]. 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 [11,13,14,44]. 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.

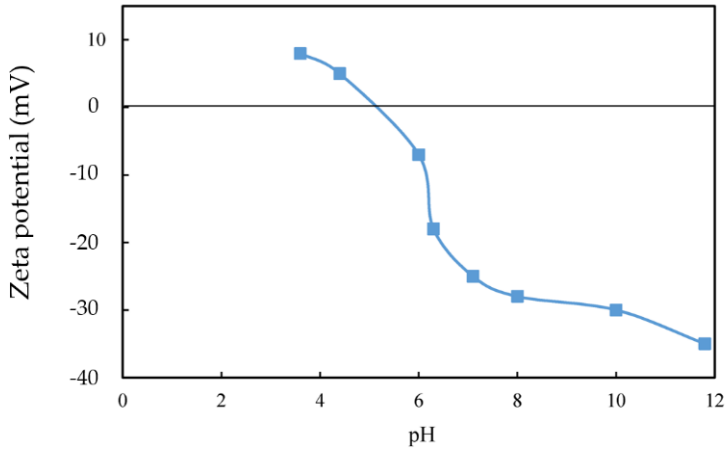

Figure 2. Zeta potential as a function of pH, adapted from Filippov et al. [42].

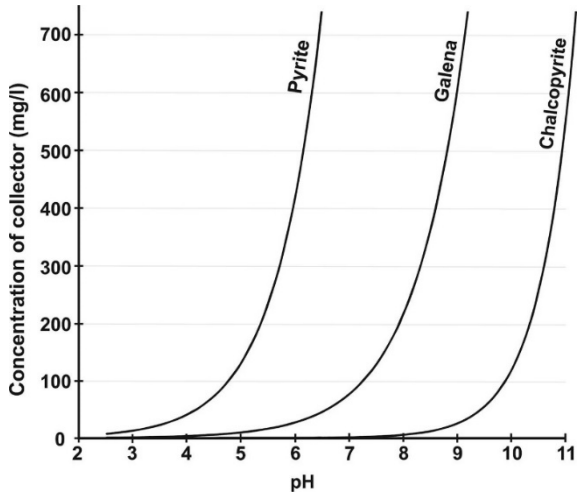

Figure 3. The effect of collector concentration and pH value in the flotation of chalcopyrite, pyrite and galena, adapted from Wark and Cox [43].

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 [5,6,13–16].

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 [5,6,15,16].

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 [45]. 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 [12].

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 [46], 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.

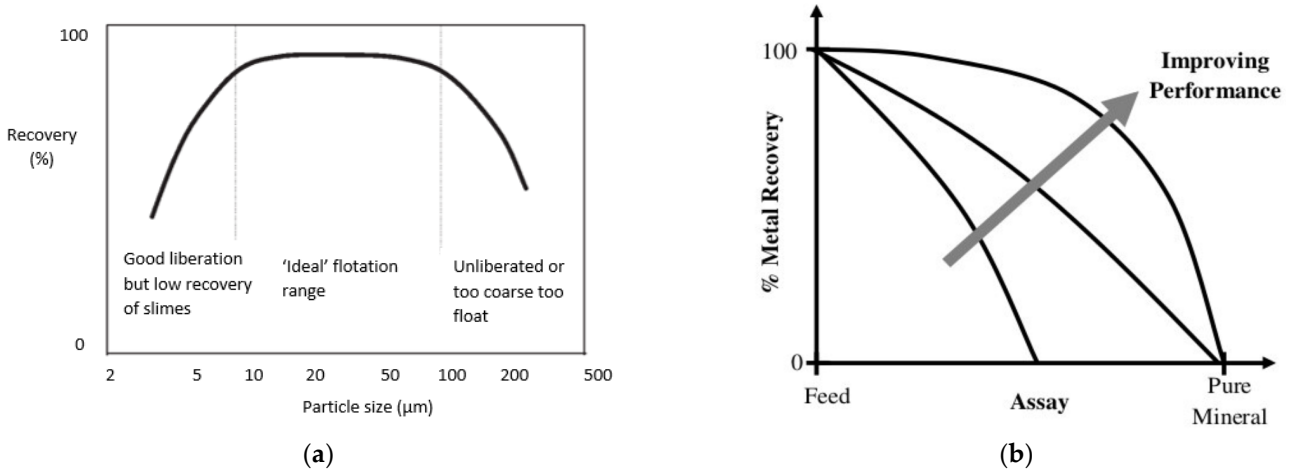

Figure 4. (**a**) Typical recovery–particle size curve, adapted from Pearse [47]; (**b**) typical recovery-grade curve, adapted from Klassen and Mokrousov [48].

Although considerable success has been achieved, sustainable froth flotation using chemical reagents is becoming more challenging [48]. High-grade ores are diminishing, and consequently gangue content is increasing [48]. Furthermore, mineral-bearing ores are becoming more complex [49]. Therefore, the amount of flotation reagents required for effective flotation is continually increasing. It has been reported [49] 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 [5,6,13–16]. 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.

4. 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.

4.1. 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* [50]. The presence of microorganisms and their metabolic products alters the mineral surfaces, resulting in flotation or flocculation [2]. 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 [51]. 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 [51]. The bioprotein that induces hydrophobicity on mineral surfaces is secreted by bacteria [52]. 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.

4.2. Paenibacillus polymyxa

Separation of chalcopyrite from pyrite has also been achieved with the use of *Paenibacillus polymyxa* cells, which preferentially depressed pyrite [44]. 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 [44], 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 [53]. 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 [53].

4.3. Mycobacterium phlei

The highly hydrophobic bacteria *Mycobacterium phlei* was found to selectively attach to coal and not to pyrite [54]. The hydrophobicity so induced led in turn to clustering of coal particles, promoting flocculation. Similar results [55] 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 [19]. Subsequently, column flotation tests were done to further separate coal from contaminants such as

pyrite [55]. The results from the studies with *M. phlei* in coal cleaning [19,54] 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.

4.4. 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 [56]. The bacterium preferentially attaches to the pyrite surfaces, rendering the mineral hydrophilic [10,57]. The use of *A. ferrooxidans* reduced pyrite floatability by ~70%. Another study [18] observed depression of pyrite by *A. ferrooxidans*, leading to a 50% reduction in pyrite recovery.

In much earlier studies [58], an 80% reduction in pyrite floatability was reported. The results by Nagaoka et al. [10] 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* [18]. 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 [59]. However, an earlier study [60] 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. [2], 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 [61]. 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 [62]. 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 [63]. A conditioning time of 20 min was recommended for effective pyrite suppression [62]. The conditioning should be done in a medium containing soluble ferrous ions that are used as a growth substrate for *A. ferrooxidans* [64]. Simultaneous interaction of minerals with bacterial cells and collector was also recommended [56].

Similar results were also observed for the separation of pyrrhotite and chalcopyrite using *A. ferrooxidans* [9]. *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 [9], as well as due the reaction of Cu from the chalcopyrite with the xanthate molecules, as reported in previous work [65,66], 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 [9]. Although contact angle values were not given [9], values of up to 80° are required for high hydrophobicities. Figure 5 [9] shows the effects of *A. ferrooxidans* on chalcopyrite and pyrrhotite.

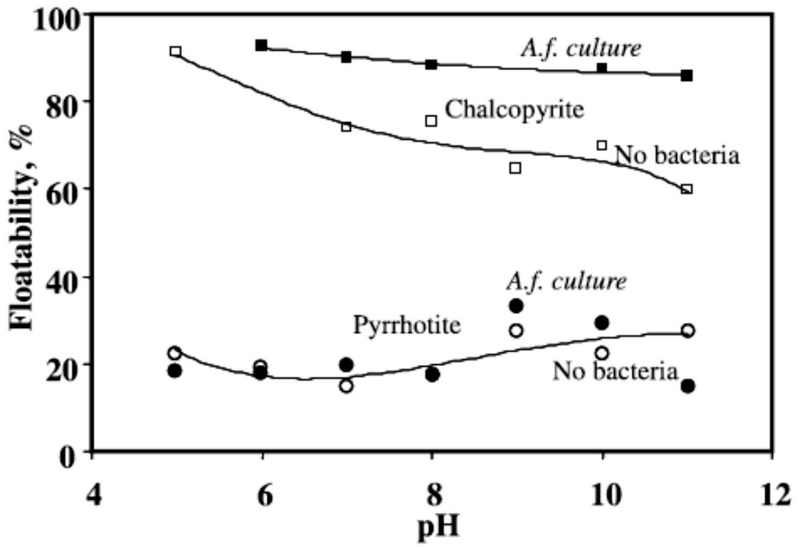

Figure 5. Floatability of chalcopyrite and pyrrhotite in the presence of a collector with (solid symbols) and without bio-modification (open symbols). Adapted from Pecina-Treviño et al. [9].

Although *A. ferrooxidans* is acidophilic, it has been proven that it can function as a pyrite depressant at higher pH (of ~8) values [67]. The increase in the depressing capability of *A. ferrooxidans* has been attributed to the increase of bacterial attachment density on pyrite [68]. 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 [68]. 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 [67]. 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 [4]. The pH for pyrite depression is close to that reported for PGM flotation, i.e., a pH of 9 [69]. 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 [4]. The adapted culture would then be separated from pyrite slurries by filtration and used for bioconditioning of pyrite flotation slurries.

In another study [70], 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 [67]. Production of EPS is not a function of pH [67], 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 [64].

4.5. Acidithiobacillus thiooxidans

Separation of pyrite and chalcopyrite has been done using *Acidithiobacillus thiooxidans* [11,62]. It was possible to separate chalcopyrite from pyrite under both acidic and neutral conditions [11]. 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 [71]. However, *A. thiooxidans* (and *A. ferrooxidans*), if not adapted, do not thrive well in the presence of Cu ions at high concentrations [9,11,72], 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.

4.6. Leptospirillum ferrooxidans

Leptospirillum ferrooxidans has been reported to be useful in the separation of pyrite and chalcopyrite [63]. *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 [63]. 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 [63]. 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* [63]. On the other hand, the best separation was obtained when *L. ferrooxidans* grew on chalcopyrite [73]. The contradictory flotation results between the different studies [63,73] 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 [73]. 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 [67,74,75].

The recovery of chalcopyrite in the presence of *L. ferrooxidans* has been reported by Diaz-Lopez et al. [76]. They, however, found that the recovery of chalcopyrite decreased in the presence of pyrrhotite [76]. The presence of pyrrhotite results in galvanic interactions with chalcopyrite [76]. 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 [76]. In another study [77] 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 [62].

4.7. Bacillus subtilis

Bacillus subtilis was found to have a depressing effect on pyrite [78]. 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. [78], 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 [78].

4.8. Bacillus pumilus and Alicyclobacillus ferrooxidans

Bacillus pumilus and *Alicyclobacillus ferrooxidans* have been found to act as both collectors and depressants for pyrite [12]. 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.

4.9. Halophilic Bacteria

Halophilic bacteria have been successfully used as a substitute for lime as a depressant of pyrite, promoting the selective flotation of chalcopyrite [79]. 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 [67].

4.10. 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 [61]. 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.

4.11. 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 [80]. 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.

4.12. 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 [2] 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 [64]. 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 [61]. 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 [61]. 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 [80] could also be used for the biobeneficiation of

pentlandite. However, it cannot be postulated whether these would promote flotation or act as a depressant.

5. Removal of Silicates and Chromites during Biobeneficiation

It is well known that PGM ores are associated with silicates and chromite as gangue materials and that these should be removed during beneficiation to ensure efficiency of the subsequent processes, whether hydrometallurgical or pyrometallurgical. It is known that siliceous species increase reagent consumption during leaching processes, while the presence of chromite increases the smelting costs of PGMs. *Paenibacillus polymyxa* has been found to induce hydrophobicity to silica [8]. Thus, the use of *Paenibacillus polymyxa* may be used to concentrate PGMs by reverse flotation.

A. ferrooxidans favors the flotation of sulphide minerals (other than pyrite) as a result of elemental sulphur formation [61]. It is therefore likely that the use of ferro-oxidans might result in the concentration of PGMs with the associated base metal minerals, leaving behind the non-sulphide gangue (silica and chromite). Sulphate-reducing bacteria may also be useful for the separation of PGMs from silica and chromite, as they have been reported to either cause flotation or depression of chalcopyrite as a result of either sulphide generation or the H_2S depressant [61], neither of which can be formed from either silica or chromite.

Another option for the removal of silica is the use of silicate-destroying bacteria, such as the mucilaginous strains [81], prior to flotation. The metabolites produced by the *Bacillus mucilaginous* strains were responsible for the leaching of silicate ores [82]. Bacillus strains have been reported to be responsible for the release of sulphidic minerals from aluminosilicates [82]. Therefore, these strains can be used for upgrading the PGM- and base metal-bearing sulphide content prior to bioflotation.

Tables 5 and 6 provide a summary of all the microorganisms involved in the biobeneficiation of PGM associated minerals. The information in Tables 5 and 6 may be useful for PGM biobeneficiation. A detailed mineralogical analysis would reveal the mineral associations, and Tables 5 and 6 would provide information regarding the suitable bacteria and conditions for beneficiation. Based mainly on the information from Tables 5 and 6, the proposed parameters for the bioflotation of PGMs are shown in Table 7, and are compared to those for conventional flotation. It can be deduced from Table 7 that the parameters for bioflotation of PGMs are comparable to those for conventional PGM flotation, with the advantage of being applicable to low-grade PGM ores.

Table 5. Bacteria involved in the flotation of PGM associated minerals and the corresponding conditions.

Bacteria	PGM Associated Mineral Floated	PGM Associated Mineral Depressed	Bioflotation Conditions and BMS Recovery or Depression	References
Bacillus polymyxa		Pyrite	pH—8 (hexamine collector—1×10^{-4} M) bio-conditioning time—15 min, extracellular bacterial protein—50 mg/L, up to 92.2% pyrite depressed	[50]
Paenibacillus polyxyma	Chalcopyrite	Pyrite	particle size—106 + 38 µm, 1 min, air flow rate—13 Lh^{-1}, pH 3–10, 3×10^6 cells mL^{-1}, up to 65% chalcopyrite recovered and up to 70% pyrite depressed	[44,51]
Acidithiobacillus ferrooxidans	Chalcopyrite	Pyrite	methyl isobutyl carbinol collector, aeration—100 mL/min Conditioning time—20 min, Flotation time—10 min Cell suspension added to 10 mL KPO_4, pH 2–8, 72% to 100% chalcopyrite floated and 77% to 95% pyrite depressed	[4,10,56–58,62,64,67,70]
Leptospirillum ferrooxidans	Pyrite	Chalcopyrite	potassium isopropyl xanthate collector, preconditioning time (30 min), 2.5×10^8 cells mL^{-1}, pH 4, 67% pyrite recovery and 75% chalcopyrite depression	[63]
Leptospirillum ferrooxidans	Chalcopyrite	Pyrrhotite	Conditioning time (10 min), conditioning substrate (thionocarbamate) isopropyl ethyl thionocarbamate collector, nitrogen injected, time (10 min), chalopyrite recovery increased to between 80% and 95%, 30% pyrrhotite depressed	[76]
Bacillus subtilis	-	Pyrite	Incubation period (1 h), flotation time (3 min), 79%–94% pyrite depressed	[78]
Bacillus pumilus	-	Pyrite	10% vol/vol inoculum, 25% wt/vol pyrite, 25% pulp density, 150 rpm agitation, 30 °C, varying pH, 14–21 days, (no recoveries reported) contact angle of about 5°	[12]

Table 5. *Cont.*

Bacteria	PGM Associated Mineral Floated	PGM Associated Mineral Depressed	Bioflotation Conditions and BMS Recovery or Depression	References
Bacillus pumilus	Pyrite	No information	10% vol/vol inoculum, 25% wt/vol pyrite, 25% pulp density, 150 rpm agitation, 30 °C, varying pH, 0–14 days, (no recoveries reported) contact angles between 90 and 100°	[12]
Alicyclobacillus ferrooxidans	-	Pyrite	10% vol/vol inoculum, 25% wt/vol pyrite, 25% pulp density, 150 rpm agitation, 30 °C, varying pH, 14 days, (no recoveries reported) contact angle of about 68°	[12]
Alicyclobacillus ferrooxidans	Pyrite	No information	10% vol/vol inoculum, 25% wt/vol pyrite, 25% pulp density, 150 rpm agitation, 30 °C, varying pH, 4–8 days, (no recoveries reported) contact angles between 80 and 85°	[12]
Halophilic bacteria (*Halomonas boliviensis*, *Halobacillus* sp. and *Halomonas* sp.)	Chalcopyrite	Pyrite	pH (between 8.02 and 8.14), mineral particle size (100–200 µm), Sodium Isopropyl Xanthate (SIPX), flotation time (5 min), up to 91% chalcopyrite flotation and 90% pyrite depression	[79]
Sulphate-reducing bacteria (*Desulfovibrio*)	-	Chalcopyrite	pH (6–7), H_2S gas production (no extraction information provided)	[61]
Sulphate-reducing bacteria (*Desulfovibrio*)	Chalcopyrite	-	Sulphide products formation, no extraction information provided	[61]
Mixed bioleaching cultures (*A. ferrooxidans*, *A. thiooxidans* and *L. ferrooxidans*)	Chalcopyrite	Pyrite	Used EPS extracted from chalcopyrite-rich concentrate, pH (4 and 9), sodium isobutyl xanthate, flotation time (20 min), 70 °C, up to 80% chalcopyrite recovered and about 75% pyrite depressed	[80]

Table 6. Bacteria involved in the flocculation of PGM associated minerals and the corresponding conditions.

Bacteria	PGM Minerals Recovered by Flocculation	Flocculation Conditions and Associated Recoveries	Reference
Bacillus polymyxa	Pyrite	pH 3 20 min, 50 mg/L metabolite-extracted protein d50 < 50 μm, 92% pyrite settled	[50,51]
Mycobacterium phlei	Pyrite (by reverse recovery)	pH (2–11), bacterial concentration (200 ppm), 64% pyrite rejection	[19]
Acidithiobacillus ferrooxidans	Pyrite	pH adjusted by NaOH and H_2SO_4, double distilled water medium, 2 min settling time, 1.8×10^8 cells/mL, pulp density of 1 g/100 mL, various pH, about 98% pyrite settled	[64]
Acidithiobacillus thiooxidans	Pyrite	pH adjusted by NaOH and H_2SO_4, double distilled water medium, 2 min settling time, 1.8×10^8 cells/mL, pulp density of 1 g/100 mL, various pH, about 78%–96% pyrite settled	[64]
Leptospirillum ferrooxidans	Chalcopyrite	Solid concentration (2.5 g/L), Particle size (<5 μm), Bacterial concentration (4×10^{10} cells/g), about 100% chalcopyrite settled	[63]
Bacillus subtilis	Pyrite	100 mL cell suspension in 10^{-3} M KNO_3, Sample particle size (5–8 μm), up to 85% pyrite settled	[78]

Table 7. Proposed parameters for PGM bioflotation and those used in conventional PGM flotation.

Parameter	Proposed for Bioflotation of PGMs	Used in Conventional Flotation of PGMs
Grade	<3 g/t	3–8 g/t [38]
Particle size	<50 µm	38–75 µm [25]
Temperature	30 °C	~25 °C [83]
pH	8	9 [69]
Pulp density	25% (*w/v*)	30–35% (*w/v*) [25,83]

6. Potential Challenges and Opportunities of PGM Biobeneficiation

Conventional froth flotation processes are associated with such challenges as environmental pollution and the depletion of high-grade ores. Given the good economics and environmental friendliness of biobeneficiation, it presents an attractive alternative to the use of conventional chemical froth flotation processes on the depleting PGMs. However, there are potential challenges that ought to be overcome. To begin with, biobeneficiation of PGMs has not been specifically investigated, and there is still need for practical investigation of the effects of microorganisms in the biobeneficiation of PGMs.

It is well known that when ores are mined, there is significant variability in terms of their chemical and physical characteristics. Variations in the chemical characteristics of ores are a threat to achieving consistent separation during PGM biobeneficiation. As reported by Rao et al. [84], intensified efforts will be required to fully understand the difference in behaviour of the various PGM-bearing mineral species during the biobeneficiation process.

Although biobeneficiation units present a more economically attractive option than conventional chemical froth flotation processes, the diminishing grades and comminution costs remain hurdles to be considered in the economics of PGM biobeneficiation. The need to complement microorganisms with conventional chemicals is also a potential obstacle to the economics of bioflotation processes. Furthermore, culturing of microorganisms and the potential need for high inoculum dosages might also compromise the overall economics of PGM bioflotation. It has been reported that there might be a need to include fermenters and associated equipment in the biobeneficiation process [3], and this has the potential to significantly enhance capital costs.

In addition to economics-related challenges, biobeneficiation of PGMs is associated with several operational challenges. Along with most ores, PGM ores are often chemically and physically heterogeneous such that process control and optimisation may be a challenge. It has been reported that the adsorption of microorganisms on mineral surfaces is pH-dependent [2]. Therefore, pH control may be required for PGM biobeneficiation. It has been reported that the best bacterial growth conditions are needed for optimum separation of chalcopyrite and pyrite, which are associated with PGMs [3]. As such, the need to establish the optimum microbial growth conditions for efficient PGM beneficiation is likely to be a challenge that needs consideration. As mentioned in the work by Raichur et al. [19], pyrite entrapped in agglomerated coal particles leads to ineffective separation of the two mineral species. It is likely that the same challenge may be encountered during bioflocculation of PGMs among the various mineral species. The toxicity of chalcopyrite towards microorganisms is also a potential challenge in the beneficiation of PGMs.

It is, however, important to note that a number of the potential challenges to the biobeneficiation of PGMs are encountered during conventional froth flotation processes as well. For example, challenges to do with ore heterogeneity, comminution costs, process control, selectivity, and investing in equipment are also hurdles in conventional chemical processes. Therefore, these challenges are likely to be surmountable.

The scientific basis for the potential of biobeneficiation of PGMs is their close association with mineral sulphides such as chalcopyrite that have been successfully floated or depressed using microorganisms. These microorganisms are biodegradable, non-pathogenic and non-toxic, such that successful development of PGM biobeneficiation processes will go a long way in contributing to sustainable mineral extraction. Most of the microorganisms

that have been used in the beneficiation of sulphide minerals associated with PGMs are omnipresent, and therefore it will be possible to generate a high yield of microorganisms for PGM beneficiation.

The microorganisms that have been used for the biobeneficiation of the mineral sulphides associated with PGMs are well understood. The mineralogy of the various PGM deposits is also well understood. Since biobeneficiation mainly depends on the interaction between minerals and microorganisms, there is therefore significant potential for the biobeneficiation of PGMs. Furthermore, recent advances in genetic engineering and DNA technologies can be leveraged in the development of the most suitable microbial combinations for PGM beneficiation. With genetic engineering, it is possible to develop function-specific strains. As such, there is great potential for using suitable genetically modified bacterial strains for the beneficiation of PGMs. To achieve this, there is a need for collaborative efforts between microbiologists and mineral processing engineers. The potential for beneficiation of PGMs can be further derived from the emergence of the field of Data Sciences. Data Science provides the tools to harness data and generate machine learning models that can be inputted for process control. Data Science comes with version control systems such as GIT and GITHUB, which allow for unlimited collaboration as well as tools for model evaluation and refinement. Therefore, by leveraging on the fields of Data Analytics, Data Science and Data Engineering, it should be possible to generate data during microbe–PGM interaction and use this data to create models that can in turn be used for biobeneficiation process control.

7. Conclusions

This paper has demonstrated the immense potential of the biobeneficiation of PGMs. Biobeneficiation of the sulphide minerals closely associated with PGMs has been carried out and the conditions are well known. As discussed, several different microbial species can be employed in the biobeneficiation of associated base metal sulphides. Bacterial microorganisms have been successfully used for both bioflotation and bioflocculation at pH conditions between 6 and 9 and temperatures around 30 °C. These pH and temperature conditions imply that it is possible to manage both corrosion issues and energy costs associated with biobeneficiation. Bacteria such as *Bacillus polymyxa*, *Mycobacterium phlei*, *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, *Paenibacillus polymyxa*, and *Bacillus subtilis* are suitable for both bioflotation and bioflocculation. The use of EPS derived from these microorganisms has also been reported for biobeneficiation. The advantage of using the EPS is that their production is not dependent on pH, and they have been reported to have better attachment at the mineral surfaces than their parent microorganisms. In conventional PGM flotation, for example, the flotation behavior of the associated sulphides determines overall PGM recovery. The same principle can be extended to PGM bioflotation, as the bio-flotation behavior of associated sulphides is well understood. Although, there are potential challenges in the biobeneficiation of PGMs, a number of these challenges are common to the conventional processes; thus, lessons from conventional processes can be applied to circumvent these challenges. The potential of PGM biobeneficiation also lies in the recent advances in biotechnology such that, apart from the already known microorganisms, genetically modified strains can be developed. Furthermore, the advent of Data Engineering provides an additional tool for the development of processes suitable for the biobeneficiation of PGMs.

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References

1. Watson, J.H.P.; Ellwood, D.C. Biomagnetic separation and extraction process for heavy metals from solution. *Miner. Eng.* **1994**, *7*, 1017–1028. [CrossRef]
2. Chandraprabha, M.N.; Natarajan, K.A. Microbially induced mineral beneficiation. *Miner. Process. Extr.* **2009**, *31*, 1–29. [CrossRef]
3. Smith, R.W.; Miettinen, M. Microorganisms in flotation and flocculation: Future technology or laboratory curiosity? *Miner. Eng.* **2006**, *19*, 548–553. [CrossRef]
4. 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. [CrossRef]
5. 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. [CrossRef]
6. 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. [CrossRef]
7. Santhiya, D.; Subramanian, S.; Natarajan, K.A.; Rao, K.H.; Forssberg, K.S.E. Bio-modulation of galena and sphalerite surfaces using *Thiobacillus thiooxidans*. *Int. J. Miner. Process.* **2001**, *62*, 121–141. [CrossRef]
8. Natarajan, K.A.; Deo, N. Role of bacterial interaction and bioreagents in iron ore flotation. *Int. J. Miner. Process.* **2001**, *62*, 143–157. [CrossRef]
9. 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. [CrossRef]
10. Nagaoka, T.; Ohmura, N.; Saiki, H. A novel mineral flotation process using *Thiobacillus ferrooxidans*. *Appl. Environ.* **1999**, *65*, 3588–3593. [CrossRef]
11. 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. [CrossRef]
12. 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. [CrossRef]
13. 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. [CrossRef]
14. Patra, P.; Natarajan, K.A. Role of mineral specific bacterial proteins in selective flocculation and flotation. *Int. J. Miner. Process.* **2008**, *88*, 53–58. [CrossRef]
15. Vasanthakumar, B.; Ravishankar, H.; Subramanian, S. A novel property of DNA—As a bioflotation reagent in mineral processing. *PLoS ONE* **2012**, *7*, e39316. [CrossRef] [PubMed]
16. 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. [CrossRef]
17. Mehrabani, J.V.; Mousavi, S.M.; Noaparast, M. Evaluation of the replacement of NaCN with *Acidithiobacillus ferrooxidans* in the flotation of high-pyrite, low-grade lead–zinc ore. *Sep. Purif. Technol.* **2011**, *80*, 202–208. [CrossRef]
18. 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.
19. 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. [CrossRef]
20. Marhual, N.P.; Pradhan, N.; Kar, R.N.; Sukla, L.B.; Mishra, B.K. Differential bioleaching of copper by mesophilic and moderately thermophilic acidophilic consortium enriched from same copper mine water sample. *Bioresour. Technol.* **2008**, *99*, 8331–8336. [CrossRef]
21. Buswell, A.M.; Bradshaw, D.J.; Harris, P.J.; Ekmekci, Z. The use of electrochemical measurements in the flotation of a platinum group minerals (PGM) bearing ore. *Miner. Eng.* **2002**, *15*, 395–404. [CrossRef]
22. Buswell, A.M.; Nicol, M.J. Some aspects of the electrochemistry of the flotation of pyrrhotite. *J. Appl. Electrochem.* **2002**, *32*, 1321–1329. [CrossRef]
23. Kim, G.; Park, K.; Choi, J.; Gomez-Flores, A.; Han, Y.; Choi, S.Q.; Kim, H. Bioflotation of malachite using different growth phases of *Rhodococcus opacus*: Effect of bacterial shape on detachment by shear flow. *Int. J. Miner. Process.* **2015**, *143*, 98–104. [CrossRef]
24. Cramer, L.A. What is your PGM concentrate worth. In Proceedings of the Third International Platinum Conference, Platinum in Transformation, Southern African Institute of Mining and Metallurgy, Sun City, South Africa, 6–9 October 2008; pp. 387–394.
25. Corin, K.C.; McFadzean, B.J.; Shackleton, N.J.; O'Connor, C.T. Challenges Related to the Processing of Fines in the Recovery of Platinum Group Minerals (PGMs). *Minerals* **2021**, *11*, 533. [CrossRef]
26. Scoon, R.N.; Teigler, B. Platinum-group element mineralization in the critical zone of the western Bushveld Complex; I, Sulfide poor-chromitites below the UG-2. *Econ. Geol.* **1994**, *89*, 1094–1121. [CrossRef]
27. Naldrett, A.J.; Naldrett, A.L. *Magmatic Sulfide Deposits: Geology, Geochemistry and Exploration*; Springer Science & Business Media: Berlin, Germany, 2004.
28. Junge, M.; Oberthür, T.; Melcher, F. Cryptic variation of chromite chemistry, platinum group element and platinum group mineral distribution in the UG-2 chromitite: An example from the Karee Mine, western Bushveld Complex, South Africa. *Econ. Geol.* **2014**, *109*, 795–810. [CrossRef]

29. Junge, M.; Oberthür, T.; Osbahr, I. Gutter, Platinum-group elements and minerals in the lower and middle group chromitites of the western Bushveld Complex, South Africa. *Miner. Depos.* **2016**, *51*, 841–852. [CrossRef]
30. Barnes, S.J.; Pagé, P.; Prichard, H.M.; Zientek, M.L.; Fisher, P.C. Chalcophile and platinum-group element distribution in the Ultramafic series of the Stillwater Complex, MT, USA—Implications for processes enriching chromite layers in Os, Ir, Ru, and Rh. *Miner. Depos.* **2016**, *51*, 25–47. [CrossRef]
31. Kinloch, E.D. Regional trends in the platinum-group mineralogy of the critical zone of the Bushveld Complex, South Africa. *Econ. Geol.* **1982**, *77*, 1328–1347. [CrossRef]
32. Oberthür, T.; Weiser, T.W.; Gast, L.; Kojonen, K. Geochemistry and mineralogy of platinum-group elements at Hartley Platinum Mine, Zimbabwe. *Miner. Depos.* **2003**, *38*, 327–343. [CrossRef]
33. Holwell, D.A.; Boyce, A.J.; McDonald, I. Sulfur isotope variations within the Platreef Ni-Cu-PGE deposit: Genetic implications for the origin of sulfide mineralization. *Econ. Geol.* **2007**, *102*, 1091–1110. [CrossRef]
34. Osbahr, I.; Klemd, R.; Oberthür, T.; Brätz, H.; Schouwstra, R. Platinum-group element distribution in base-metal sulfides of the Merensky Reef from the eastern and western Bushveld Complex, South Africa. *Miner. Depos.* **2013**, *48*, 211–232. [CrossRef]
35. Junge, M.; Wirth, R.; Oberthür, T.; Melcher, F.; Schreiber, A. Mineralogical siting of platinum-group elements in pentlandite from the Bushveld Complex, South Africa. *Miner. Depos.* **2015**, *50*, 41–54. [CrossRef]
36. 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. [CrossRef]
37. Seymour, R.J.; O'Farrelly, J.I.; Potter, L.C. Platinum-group metals. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley and Sons: New York, NY, USA, 2000.
38. Schouwstra, R.P.; Kinloch, E.D.; Lee, C.A. A short geological review of the Bushveld Complex. *Platin. Met. Rev.* **2000**, *44*, 33–39.
39. Lee, C.A. A review of mineralization in the Bushveld Complex and some other layered intrusions. *Dev. Petrol.* **1996**, *15*, 103–145.
40. 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.
41. 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.
42. 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. [CrossRef]
43. Wark, I.W.; Cox, A.B. Principles of flotation, III. *Trans. AIME* **1934**, *112*, 267–301.
44. 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. [CrossRef]
45. 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.
46. Sheni, N.; Corin, K.; Wiese, J. Considering the effect of pulp chemistry during flotation on froth stability. *Miner. Eng.* **2018**, *116*, 15–23. [CrossRef]
47. Pearse, M.J. An overview of the use of chemical reagents in mineral processing. *Miner. Eng.* **2005**, *18*, 139–149. [CrossRef]
48. Klassen, V.I.; Mokrousov, V.A. *An Introduction to the Theory of Flotation*; Butterworth: Oxford, UK, 1963.
49. Bulatovic, S.M. *Handbook of Flotation Reagents: Chemistry, Theory and Practice: Volume 1: Flotation of Sulfide Ores*; Elsevier: Amsterdam, The Netherlands, 2007.
50. Patra, P.; Natarajan, K.A. Microbially-induced flocculation and flotation for pyrite separation from oxide gangue minerals. *Miner. Eng.* **2003**, *16*, 965–973. [CrossRef]
51. 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. [CrossRef]
52. 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. [CrossRef] [PubMed]
53. 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. [CrossRef]
54. 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. [CrossRef]
55. Raichur, A.M.; Misra, M.; Smith, R.W. Differential adhesion of hydrophobic bacteria onto coal and associated minerals. *Coal Prep.* **1995**, *16*, 51–63. [CrossRef]
56. 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. [CrossRef]
57. 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. [CrossRef]
58. 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. [CrossRef]

59. Blake II, R.C.; Sasaki, K.; Ohmura, N. Does aporusticyanin mediate the adhesion of *Thiobacillus ferrooxidans* to pyrite? *Hydrometallurgy* **2001**, *59*, 357–372. [CrossRef]
60. Misra, M.; Chen, S. The effect of growth medium of *Thiobacillus ferrooxidans* on pyrite and galena flotation. *Miner. Eng.* **1996**, *9*, 157–168. [CrossRef]
61. 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.
62. 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. [CrossRef]
63. 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. [CrossRef]
64. 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. [CrossRef]
65. Abramov, A.; Avdohin, V.M. *Oxidation of Sulfide Minerals in Benefication Processes*; Gordon and Breach Science Publishers: Amsterdam, The Netherlands, 1998.
66. 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.
67. San Martín, F.; Kracht, W.; Vargas, T. Biodepression of pyrite using *Acidithiobacillus ferrooxidans* in seawater. *Miner. Eng.* **2018**, *117*, 127–131. [CrossRef]
68. San Martín, F.; Kracht, W.; Vargas, T.; Rudolph, M. Mechanisms of pyrite biodepression with *Acidithiobacillus ferrooxidans* in seawater flotation. *Miner. Eng.* **2020**, *145*, 106067. [CrossRef]
69. 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.
70. 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. [CrossRef]
71. Jefferson, K.K. What drives bacteria to produce a biofilm? *FEMS Microbiol. Lett.* **2004**, *236*, 163–173. [CrossRef]
72. 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. [CrossRef] [PubMed]
73. 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. [CrossRef]
74. 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. [CrossRef]
75. 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. [CrossRef]
76. 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. [CrossRef]
77. 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. [CrossRef]
78. 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. [CrossRef]
79. 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. [CrossRef]
80. Govender, Y.; Gericke, M. Extracellular polymeric substances (EPS) from bioleaching systems and its application in bioflotation. *Miner. Eng.* **2011**, *24*, 1122–1127. [CrossRef]
81. Sun, D.S.; Wan, Q.; Zhao, X.P.; Zhang, Q. Metabolites of *Bacillus mucilaginous* JXF and their desiliconization Effect. *J. Min. Metall. Eng.* **2008**, *28*, 52–56.
82. Štyriaková, I.; Bhatti, T.M.; Bigham, J.M.; Tyriak, I.; Vuorinen, A.; Tuovinen, O.H. Weathering of phlogopite by *Bacillus cereus* and *Acidithiobacillus ferrooxidans*. *Can. J. Microbiol.* **2004**, *50*, 213–219. [CrossRef]
83. Sefako, R.; Sibanda, V.; Sekgarametso, K. PGM extraction from oxidized ores using flotation and leaching. *J. S. Afr. Inst. Min. Metall.* **2019**, *119*, 929–936. [CrossRef]
84. Rao, K.H.; Vilinska, A.; Chernyshova, I.V. Minerals bioprocessing: R & D needs in mineral biobeneficiation. *Hydrometallurgy* **2010**, *104*, 465–470.