minerals

Review

Recent Developments in Microbiological Approaches for Securing Mine Wastes and for Recovering Metals from Mine Waters

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Abstract: Mining of metals and coals generates solid and liquid wastes that are potentially hazardous to the environment. Traditional methods to reduce the production of pollutants from mining and to treat impacted water courses are mostly physico-chemical in nature, though passive remediation of mine waters utilizes reactions that are catalysed by microorganisms. This paper reviews recent advances in biotechnologies that have been proposed both to secure reactive mine tailings and to remediate mine waters. Empirical management of tailings ponds to promote the growth of micro-algae that sustain populations of bacteria that essentially reverse the processes involved in the formation of acid mine drainage has been proposed. Elsewhere, targeted biomineralization has been demonstrated to produce solid products that allow metals present in mine waters to be recovered and recycled, rather than to be disposed of in landfill.

Keywords: acid mine drainage; biomineralization; bioremediation; bioshrouding; ecological engineering; mine tailings; sulfate-reducing bacteria
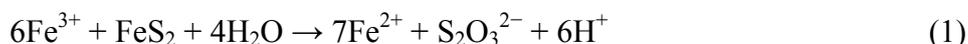
1. Introduction: Mine Water Genesis

The mining of metals and of coals generates waste materials that are potentially hazardous to the environment [1–3]. Protecting aquatic and terrestrial ecosystems from pollutants generated from mine wastes is a major concern of environmental protection bodies and the mining industry itself. Given the increasing demand by an expanding global population for metals in general and for some, such as the rare earth elements, for which new markets have arisen in recent years, it will be necessary to continue to exploit previously untapped ore bodies, though recovery of metals from other sources, such as

reprocessing mine wastes and processing electronic scrap (e-wastes) could also provide significant quantities of metals for manufacturing industries. Future developments in the metal mining industry are likely to focus on more environmentally-benign technologies that are less demanding of energy and have far smaller carbon footprints than opencast and deep-mining operations, and using pyrometallurgy to extract metals. For example, *in situ* biomining could allow target metals to be extracted from deeply-buried ore bodies without the need to hoist rocks to the surface, or to crush and mill the ore [4].

Solid waste generated by metal mining can be divided into two main categories: waste rock and mine tailings. Dumps of waste rock are composed of sand-sized particles to large boulders and have less potential to generate polluting drainage waters than tailings. The latter are fine grain wastes generated during the separation of target metal minerals from others in milled ores by froth flotation [1]. Many commercially-valuable base metals, such as copper and zinc, occur as sulfide minerals, and these are often associated in ore bodies with other, relatively non-valuable minerals, such as pyrite (FeS_2), as well as other gangue minerals. The occurrence of pyrite and other sulfide minerals in tailings wastes, as well as their fine grain size, makes them potentially highly reactive. The mechanisms involved in the oxidative dissolution of sulfide minerals have been described in many review articles and other publications (e.g., [5]). Pyrite can be oxidized by both molecular oxygen and ferric iron, the relative importance of which depends on the solubility of ferric iron, which is pH-dependent [6]. Lime is often added to suppress the flotation of pyrite, and therefore fresh mine tailings may be alkaline [1]. As pH declines, ferric iron becomes increasingly important as the main oxidant of sulfide minerals, for example in which pyrite is oxidized *via* the "thiosulfate" pathway [5]:

$$6Fe^{3+} + FeS_2 + 4H_2O \rightarrow 7Fe^{2+} + S_2O_3^{2-} + 6H^+ \tag{1}$$

For the process to continue, ferrous iron has either to be re-oxidized *in situ*, or ferric iron delivered from a more remote location. Unlike ferric iron-catalysed pyrite oxidation, the re-oxidation of the ferrous generated does require molecular oxygen and, in low pH liquors, a microbiological catalyst in the form of an acidophilic iron-oxidizing bacterium or archaeon. The thiosulfate formed in equation [1] is oxidized *via* various sulfur intermediates, to sulfuric acid, which again involves (sulfur-oxidizing) acidophilic prokaryotes, e.g.,

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \tag{2}$$

The sulfuric acid produced in this reaction not only increases the rate of sulfide mineral dissolution (by increasing the solubility of ferric iron) but also allows other cationic metals (including aluminium, and many transition metals) to be retained in solution.

2. Source Control of Mine Pollution

Acid mine waters can be generated from abandoned mine workings (deep mines and opencast operations) and from mine spoils (waste rock dumps and mine tailings). Decommissioned biomining operations (dumps and bio-heaps) can also continue to produce metal-rich acidic waters when irrigations ceases, though this is not a cause of concern in some parts of the world, e.g., in the vicinity of the Atacama Desert in northern Chile, where there are extensive copper bioleaching operations [7].

When active mining ends, pumping of groundwater is terminated and water tables rebound. The rate at which this occurs depends on climatic and other factors. In some situations, it can be a rapid

process and water levels may approach to the land surface within months of dewatering being terminated, as was the case at the Wheal Jane tin mine in Cornwall, UK, which resulted in catastrophic pollution of impacted water courses, including a marine site [8]. In contrast, water level rises in pit lakes in abandoned opencast metal mines in the more arid Iberian Pyrite Belt are relatively slow (e.g., [9]). In both cases, flooding produces water bodies that are stratified in terms of redox potentials, dissolved oxygen and other factors. Much of the water in deep mine workings and in pit lakes is anoxic [9,10] which limits the extent to which residual acid-generating minerals are oxidized.
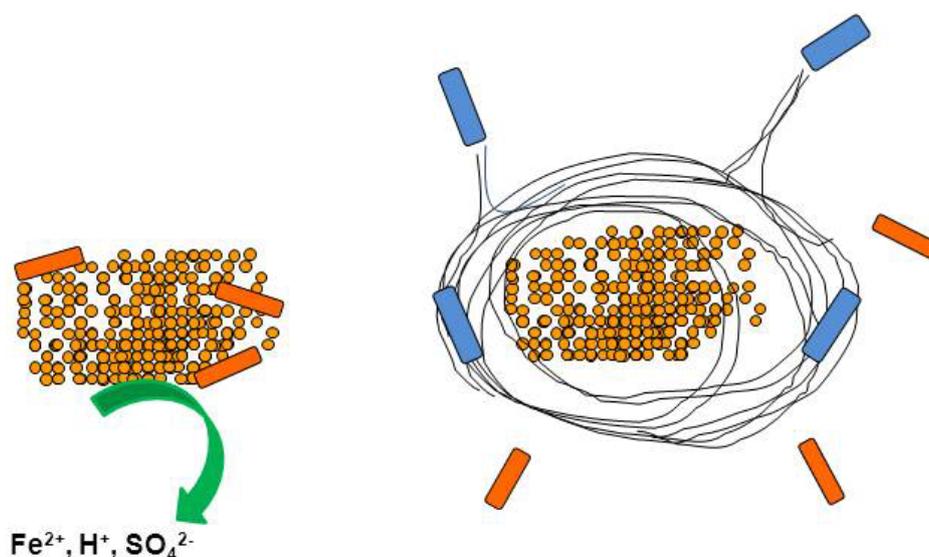
Solid wastes generated by mining and deposited at the land surface often pose more of a threat to the environment, both in the short and long term, than abandoned mine workings (e.g., [11]). Since, as noted previously, both oxygen and water are required to promote the biological oxidative dissolution of pyrite and other sulfide minerals, the engineering approaches used to control the production of acid mine drainage (AMD) from solid wastes aim to preclude access of one these essential factors [12]. In the case of waste rocks, dry covers can be used to limit water ingress [13]. Mine tailings, which are far more reactive because of their smaller grain size and generally far higher content of reactive minerals, are usually stored under water to limit contact with oxygen. Even so, ferric iron, generated in the aerobic upper water layers, can diffuse into the tailings and oxidize sulfide minerals in the absence of oxygen, as noted above. One method of limiting oxidation of mine tailings is to amend them with organic materials that are degraded by oxygen-consuming heterotrophic bacteria. Various materials have been tested, and some found to be far more effective than others. Lindsay *et al.* [14] for example found that peat was an ineffective carbon source for this purpose, whereas municipal biosolids and (especially) spent brewing grain retarded AMD production from mine tailings in a field trial site at a metal mine in Alaska.

Bacteria and archaea that catalyse the oxidative dissolution of pyritic minerals can do this without having physical contact with the mineral (non-contact leaching) but in most cases they attach to the sulfides, forming biofilms below which corrosion of the minerals progresses (contact leaching; [15]). Other bacteria that live in acidic mine waters also attach to minerals and form biofilms, including species of heterotrophic acidophiles that reduce ferric iron, rather than oxidize ferrous iron [16]. These, in theory, have a protective influence on sulfide mineral oxidation as they can control the availability of the main chemical oxidant involved at low pH (Fe^{3+}). Johnson *et al.* [17] showed that, by colonising pyrite grains by heterotrophic iron-reducing bacteria (*Acidiphilium* and *Acidocella* spp.) before exposing them to autotrophic iron- and sulfur-oxidizing acidithiobacilli, it was possible to reduce pyrite dissolution by ~80%, even under conditions deemed highly aggressive (pH < 2 and oxygen-saturated shake flask cultures). Interestingly, numbers of planktonic-phase (free-swimming) pyrite-oxidizing bacteria were far greater in cultures where the pyrite had been initially colonized with the heterotrophs, compared to fresh pyrite, the implication being that biofilm formation by the heterotrophs limited the ability of the acidithiobacilli to attach to the minerals. The technique, referred to as "bioshrouding", is illustrated in Figure 1.

Ecological engineering approaches for limiting the production of and treating AMD have gained considerable interest. Sites where mine waters display greater or lesser degrees of mitigation with no apparent anthropogenic input ("natural attenuation"), can serve as models for the design of ecologically engineered systems. One example was an acidic (pH 2.2–2.7) metal-rich stream draining an adit at a small copper mine in the Iberian pyrite belt (IPB) which had developed thick, stratified

microbial growths [18]. These appeared as green algal streamers overlying light brown and (at the lowest depth) black-coloured bacterial mats. Analysis of the mine water at the stream surface and within the microbial growths showed that a significant fraction of soluble copper generated in the aerobic mine adit was being precipitated as a solid sulfide (CuS or Cu_2S) within the black microbial mat, which contained novel acidophilic strains of sulfate-reducing bacteria (SRB). No ferrous sulfides were formed in the black mats, due to the fact that interstitial water in the mats remained extremely acidic (pH 2.9; the solubility product of CuS is many orders of magnitude lower than that of FeS). Tuttle *et al.* [19] were the first to report that SRB could be stimulated in AMD by adding organic carbon, and that their activities could promote both immobilisation of some (chalcophilic) metals and mitigation of water acidity. The IPB mine stream was, however, a site which was being (partially) attenuated naturally, since the stream received no extraneous supply of organic carbon.
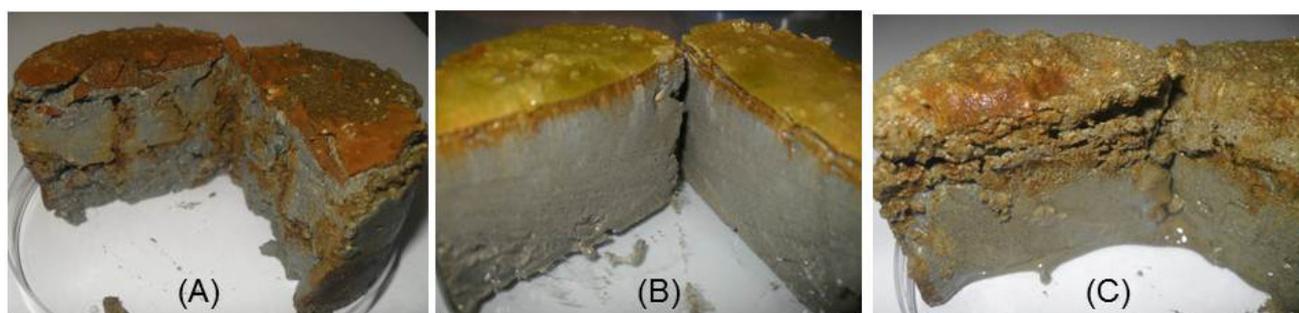
Figure 1. Schematic representation of the "bioshrouding" technique for securing mine tailings [17]. Pyrite particles (depicted in gold) colonized by iron/sulfur-oxidizing bacteria (in red), generating acid mine drainage (AMD) are shown on the left, and the same particles encased with EPS (black lines) produced by heterotrophic acidophiles (in blue) suppressing colonization by iron/sulfur-oxidizing bacteria on the right (not to scale).

Fe^{2+}, H^+, SO_4^{2-}

The assumption that the heterotrophic bacteria (including the SRB) in the microbial mats in the IPB mine drainage stream were being sustained by carbon derived from the acidophilic algae was later confirmed in laboratory experiments [20] and used as the basis of a novel ecological engineering approach for securing mine wastes [21]. The latter involved setting up 60 mesocosms containing pyrite-rich mine tailings inoculated with different species of mineral-degrading and heterotrophic bacteria (including species shown to "bioshroud" pyrite), and acidophilic micro-algae, and incubated for up to one year (Figure 2). Differences in acid genesis and metal mobilization were apparent between all inoculation regimes, with the oxidation of the mineral tailings being significantly less in mesocosms that had been inoculated with micro-algae and heterotrophic bacteria, as well as mineral-degrading acidophiles, than in others. The authors suggested an empirical method for safeguarding reactive mine tailings stored under water, in which freshly-deposited tailings are

inoculated with acidophilic micro-algae and iron- and sulfate-reducing bacteria, together with small amounts of nitrogen and phosphorus to promote their growth. This approach would allow the establishment of consortia of microorganisms that retard the oxidative dissolution of sulfide minerals, and therefore AMD production. Organic carbon (including soluble exudates) produced by the micro-algae would sustain the growth of the heterotrophic bacteria, thereby avoiding the need for continuous inputs of extraneous organic materials (Figure 3).
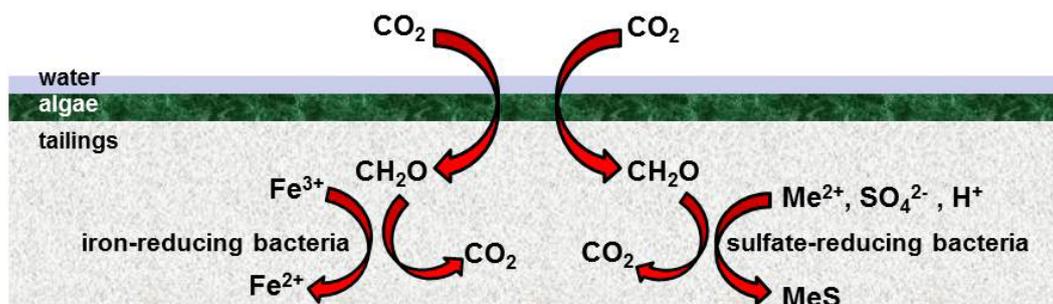
Figure 2. Mesocosms of pyritic mine tailings inoculated with mineral-oxidizing acidophilic bacteria (**A**), mineral-oxidizing and heterotrophic acidophilic bacteria and acidophilic algae (**B**) and non-inoculated controls (**C**), and incubated at 22 °C for one year [21].

3. Migration Control of Mine Pollution

Even where source control practices are in place, it is often necessary to collect and treat AMD downstream of the mine or mine spoil from which it arises. Various options are available for remediating mine waters (reviewed in [12]), which can be broadly divided into "active" and "passive" approaches. Active remediation of mine waters usually involves addition of a basic chemical reagent, such as lime (CaO) coupled with active aeration to promote oxidation of ferrous iron. Metals are precipitated chiefly as carbonates and hydroxides (and calcium as gypsum; $CaSO_4 \cdot 2H_2O$), though the water pH may have to exceed pH 8–9 to effectively remove metals such as manganese. Flocculating agents may be added to facilitate the production of "high density sludges [22]. The technology is proven and effective though expensive, and does not allow potentially valuable metals present in mine waters to be recovered and cycled. The latter is also the case for passive mine water treatment technologies (constructed wetlands, anaerobic "bioreactors" and permeable reactive barriers [12]) where biological processes are harnessed to generate alkalinity and to precipitate metals (sometimes in combination with limestone which is incorporated into the bulky organic substrate [23]). However, more recent innovative developments in mine water remediation technologies include some that facilitate the sequential and/or selective removal of soluble metals and other pollutants from AMD, thereby allowing the more valuable components to be recycled and the more toxic pollutants to be immobilized in more concentrated forms, as described below.

Figure 3. Schematic representation of an ecological engineering strategy for securing reactive mine tailings [21]. Freshly-deposited tailings are inoculated with acidophilic algae and heterotrophic bacteria. The algae grow as a surface layer on the tailings in the pond, fixing carbon and providing organic carbon (CH_2O) which sustains the growth of iron- and sulfate-reducing bacteria within the submerged tailings, thereby essentially reversing the reactions that generate AMD. Additional protection of the minerals may be mediated by "bioshrouding" by the heterotrophic acidophiles [17].

3.1. Iron

Iron is often the most abundant metal present in waters draining metal and coal mines, chiefly because of its occurrence in many sulfide minerals (e.g., chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS), pyrrhotite ($Fe_{(1-x)}S$, where x = 0 to 0.2) as well as the most abundant of all sulfides, pyrite (FeS_2)) though it can also derive from acid-catalysed dissolution of other minerals, such as chlorite $(Mg,Fe)_3(Si,Al)_4O_{10}$). Because of its intense colour, ferric iron is also responsible for the typical orange-brown pigmentation of mine water-impacted streams and sediments, making AMD one of the most obvious and readily recognized forms of water pollution.

Iron occurs as both Fe^{2+} and (complexed) Fe^{3+} in AMD. At its point of discharge from an adit draining an abandoned mine, AMD is often anoxic and iron is present almost exclusively in its more reduced ionic form, which is reflected in E_H values of <+500 mV. Chemical oxidation of ferrous to ferric proceeds slowly below pH 3.5, though iron-oxidizing prokaryotes can catalyse this reaction in mine waters that have pH values of <1.0 to >4. Ferric iron is far less soluble than ferrous, for example as a (oxy) hydroxide (Table 1) and therefore is more readily precipitated as such from mine waters. Prerequisites for this are: (i) the oxidation of ferrous iron which, as noted, is not a spontaneous chemical reaction in acidic liquors; and (ii) sufficient availability of hydroxyl (OH^-) ions, which may require addition of alkali to increase mine water pH to >3 to increase the rate of ferric iron hydrolysis. Jarosites, basic ferric iron sulfates (e.g., $KFe_3(SO_4)_2(OH)_6$) which form in extremely acidic (pH < 2) oxidized mine waters do so at rates that are too slow for effective mine water remediation.

There have been a number of reports describing the use of bacteria to accelerate the oxidation for ferrous iron as part a remediation strategy for AMD (e.g., [24–26]). The majority of studies have used the most well-known of all acidophilic iron-oxidizers, *Acidithiobacillus ferrooxidans*, often in packed-bed bioreactors. However, a study that compared different species of iron-oxidizing acidophiles concluded that an iron-oxidizing *Acidithiobacillus* (referred to at the time as a strain of *At. ferrooxidans*, though this particular isolate was subsequently reclassified as the type stain of *At. ferrivorans*) was actually the least effective of those tested, again in packed-bed bioreactors [27].
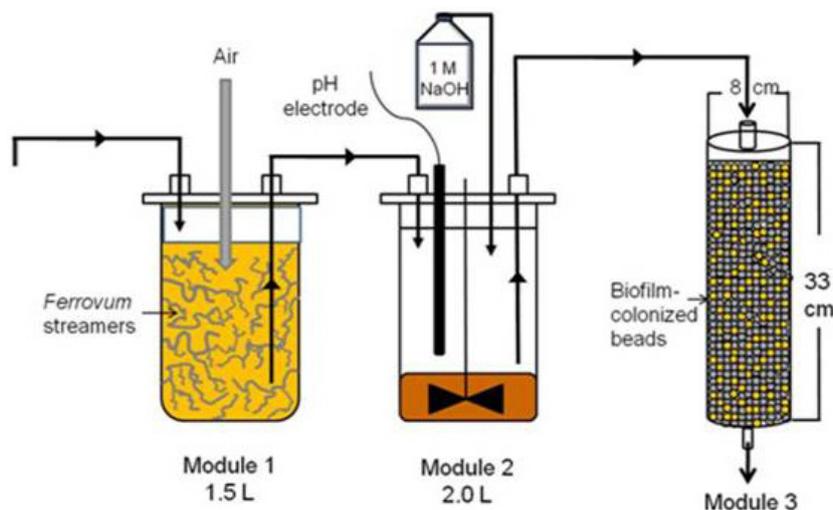
Table 1. Solubility products ($\log K_{sp}$ values at 25 °C) of hydroxides and sulfides phases of metals typically found in acid mine drainage (AMD).

Metal	Hydroxide	Sulfide
Al^{3+}	−33.5	-
Cu^{2+}	−19.8	−35.9
Fe^{2+}	−16.3	−18.8
Fe^{3+}	−38.6	-
Mn^{2+}	−12.7	−13.3
Zn^{2+}	−16.1	−24.5

Few trials using bacteria to oxidise iron and thereby facilitate the removal of soluble iron from mine waters have gone beyond the laboratory scale. One notable exception is a pilot-scale operation set up and maintained by the German company G.E.O.S., at an opencast lignite mine site at Nochten, eastern Germany [28,29]. Groundwater at the site contains ~630 mg soluble iron per litre (>99% as Fe^{2+}) which is oxidized in a continuous through-flow aerated bioreactor tank containing bacteria which are immobilized on plastic sheets. The bioreactor was initially inoculated with the more well-known iron-oxidizing acidophiles *At. ferrooxidans* and *Leptospirillum ferrooxidans*. However, very soon after the pilot plant was commissioned these bacteria were present either in very low numbers or were not detected, and bacteria related to "*Ferrovum myxofaciens*" (a more recently described iron-oxidizing acidophile [30]) and the neutrophilic iron-oxidizer *Gallionella ferruginea* [31] were the dominant bacteria present ([28,29]). The pH of the ground water was pH 4.9, but following treatment in the bioreactor this declined to pH 3.0 as a result of iron oxidation and precipitation. This relatively low pH resulted in a significant amount of the ferric iron generated (~55%) remaining in solution (aided by the fact that biological ferrous iron oxidation can be more rapid that ferric iron hydrolysis at pH 3) while the rest was precipitated as the mineral schwertmannite (idealised formula $Fe_8O_8(SO_4)(OH)_6$; [32]). Production of schwertmannite also caused the sulfate concentration of the groundwater to be lowered from 2700 to 2400 mg/L.
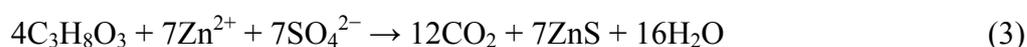
A strain of "*Fv. myxofaciens*" (PSTR) had earlier been reported to be the most effective iron-oxidizing bacterium in packed-bed bioreactor tests [27]. On the basis of this observation and the data from the Nochten plant, a laboratory-scale continuous flow reactor system for generating schwertmannite from synthetic metal mine waters was set up in which the type strain of "*Fv. myxofaciens*" (P3G) was used as the sole iron-oxidizing acidophile [33]. In contrast to the Nochten plant, which treats groundwater containing only one metal (iron) in significant concentrations, tests were carried with waters also containing aluminium, copper, manganese and zinc in order to investigate whether a "clean" schwertmannite product (*i.e.*, without other co-precipitated metals) could be generated. The modular system (Figure 4) comprised three units: a ferrous iron-oxidizing bioreactor, a schwertmannite precipitation module (in which alkali and a flocculating agent were added to the oxidized mine waters) and a packed-bed polishing unit. Over 90% of iron present in a synthetic mine water containing 280 mg Fe^{2+}/L were oxidized in the bioreactor when operated at a dilution rate of 0.41/h, and the fully-processed water contained <1 mg soluble iron/L. The schwertmannite produced was virtually free of all other metals present in the synthetic mine waters tested.

Figure 4. Schematic representation of a modular system described for precipitating iron present in waters draining metal mines as schwertmannite [33].

3.2. Selective Precipitation of Other Transition Metals

Iron is a relatively low value commodity, though schwertmannite does have potential commercial value as a pigment and as a low cost adsorbent of anions, such as arsenate and chromate ([32,34]). In contrast, other transition metals that may be present in mine drainage waters, such as copper, nickel and zinc, have higher value, and recovery and recycling of these could help off-set the costs of a an active bioremediation system. Many divalent transition metals form poorly soluble hydroxide phases, though these are have larger solubility products than those of trivalent aluminium and ferric iron (Table 1). However, an alternative approach is to precipitate chalcophilic transition metals selectively as sulfide minerals. Speciation of sulfide (H_2S, HS^- and S^{2-}) is dictated by pH, and since the species that reacts with divalent transition metals (S^{2-}) occurs in increasingly small amounts as the acidity of liquors increases, pH control can be used as a mechanism for selectively precipitating metal sulfides. Sulfate-reducing bacteria, as noted previously, use sulfate (the dominant anion in AMD) as terminal electron acceptor, generating hydrogen sulfide that can be used to precipitate chalcophilic metals and metalloids. At least two commercial systems use biosulfidogenesis to capture metals from mine waters: the *Thiopaques*® [35] and *Biosulphide*® [36] processes. However, the vast majority of SRB (and sulfur-reducing bacteria, as used in the *Biosulphide* process) are highly sensitive to acidity and need to shielded from direct contact with acidic mine waters, usually by housing them in separate reactor vessels. Some stains of acidophilic SRB have been isolated, though most currently have not yet been formally described or validated as novel species. In the first demonstration of its kind, a consortium of acidophilic SRB and other acidophiles was used to selectively precipitate copper and zinc from mine waters that also contained other dissolved metals, including aluminium and iron, using on-line bioreactors receiving direct inflow of mine water [37]. Glycerol was used as the energy source (electron donor) for the bacteria, and the generalized reaction (for precipitating zinc sulfide) is:

$$4C_3H_8O_3 + 7Zn^{2+} + 7SO_4^{2-} \rightarrow 12CO_2 + 7ZnS + 16H_2O \tag{3}$$

One of the perceived advantages of using acidophilic SRB species in an on-line reactor is that the engineering complexity of a bioremediation system can be much reduced and operating costs

minimized, which is one of the constraining factors in using active biological technologies to mitigate AMD [38].

3.3. Reduced Inorganic Sulfur Compounds and Sulfate

A variety of reduced inorganic sulfur compounds (RISCs), such as thiosulfate ($S_2O_3^{2-}$) and tetrathionate ($S_4O_6^{2-}$), are produced by several mechanisms during the (bio)processing of sulfide ores, including reactions that occur during comminution and flotation, and also as intermediates during the microbial oxidation of pyrite [5,39]. When discharged into aerated waters, RISCs are susceptible to microbial oxidation, generating sulfuric acid (e.g., Equation (2)).The combined effect of acidification and oxygen depletion means that RISC-containing waters pose a severe threat to impacted water bodies. While RISCs can be destroyed by chemical treatment, a more environmentally-benign approach is to accelerate their oxidation biologically and to neutralise the acidity generated, prior to water discharge. This has been demonstrated at 37 °C using a mixed culture of mesophilic and moderately thermophilic sulfur-oxidizing bacteria (described [40]) and at 4–10 °C using the cold-adapted bacterium *At. ferrivorans* [39].

Sulfate can occur in AMD and mine process waters in concentrations of up to hundreds of grams per litre, but since the acidity and metal/metalloid content of these waters are rightly perceived as posing greater threats to the environment, lowering sulfate concentrations has generally not been perceived as a priority issue. However, increasingly stringent regulations, such as the *European Water Framework Directive,* require concentrations of sulfate also to be below an upper limit to allow discharge of mine waters. As noted previously, some sulfate is removed (as gypsum) during active chemical treatment of AMD, and also (as schwertmannite) as part of biological iron oxidation/precipitation treatment. However, this may not be sufficient to meet regulatory demands, and techniques specifically targeting sulfate removal may be required. The *Thiopaques* process, described above, can also be used to convert soluble sulfate to soluble element sulfur [35]. This is a two-stage process that involves firstly SRB coupling the reduction of sulfate to the oxidation of an organic (e.g., ethanol) or inorganic (e.g., hydrogen) electron donor:

$$4H_2 + SO_4^{2-} \rightarrow HS^- + 3H_2O + OH^- \tag{4}$$

followed by a bacterial oxidation of hydrogen sulfide to elemental sulfur under controlled redox:

$$HS^- + O_2 + H^+ \rightarrow S^0 + H_2O \tag{5}$$

This application of the *Thiopaques* process, like that for precipitating metals, also uses neutrophilic SRB. Acidophilic SRB may also be used to remove sulfate from mine waters (using glycerol as electron donor) in on-line bioreactors maintained at pH 2.8 to 4.5 [41].

3.4. Other Metals and Metalloids

Some other metals and metalloids that occur in AMD and mine process waters may require different approaches to those described above, and again microbiological options are often available to remove them. Aluminium and manganese are usually found in relatively elevated concentrations in AMD, due to their abundance in the lithosphere and solubility in acidic liquors. Aluminium can be

precipitated as, for example, basaluminite ($Al_4(SO_4)(OH)_{10} \cdot 5(H_2O)$) at pH 5–6. The alkalinity required to increase AMD pH to that required for aluminium hydrolysis can be chemical (e.g., from addition of lime) of biological (e.g., *via* sulfate reduction or oxygenic photosynthesis) in origin. Manganese is present in AMD predominantly as Mn^{2+}, and although, like ferrous iron, it can be oxidized biologically to insoluble Mn^{4+}, this reaction is thermodynamically unfavourable below pH ~4 and proceeds slowly (unless catalysed) below pH 10. Bacteria and fungi have been shown to promote manganese oxidation and precipitation at moderately acidic pH values (>5; [42,43]), which is far lower than the pH required (> pH 8–9) to secure effective manganese removal using active (lime-based) remediation.

Arsenic is a common constituent of mine waters. At the abandoned Carnoulès metal mine in the south of France, concentrations of soluble As of up to 350 mg/L have been reported [44], while mine waters associated with gold ore processing can contain >10 g As/L [45]. Arsenic can occur both as As(III) (uncharged H_3AsO_3 at acidic pH values) and As(V) (H_2AsO4^-) in AMD. Anionic As(V) can co-precipitate with ferric iron (as scorodite; $FeAsO_4$) or be absorbed onto positively-charged particles, such as (at low pH) schwertmannite [34]. This requires As(III) to be oxidized, which may be biologically-mediated (e.g., by *Thiomonas* spp., which are abundant in Carnoulès and other moderately acidic AMD) or chemically-mediated (e.g., by ferric iron). Alternatively, As(III) may be removed by precipitation as a sulfide. Battaglia-Brunet *et al.* [45] demonstrated this using a fixed bed bioreactor colonized by SR fed continuously with an acidic (pH 2.7–5.0) solution containing 100 mg As(V)/L. Arsenic (V) was reduced to As(III) either directly or indirectly (via H_2S) by the SRB, and orpiment (As_2S_3) generated within the bioreactor. However, a switch from glycerol to hydrogen as electron donor resulted in a significant remobilization of arsenic due to the formation of soluble thioarsenic complexes.

Other metalloids, such as selenium and antimony, that are occur in mine water, though more infrequently, as oxy-anions can also be removed effectively by adsorption onto iron oxy-hydroxides, such as schwertmannite [46,47]. The fact that this ferric iron mineral can be readily produced from ferruginous mine waters in a relatively pure form (as described above) presents the opportunity in many situations of generating an effective agent for AMD remediation from the mine water itself [48].

4. Conclusions

Recent developments from research carried out with solid and liquid mine wastes have led to new opportunities to use biotechnology to secure reactive mine tailings and to selectively remove metals and other contaminants from mine drainage waters. New possibilities for the ecological engineering of mine wastes, based on mimicking environments that display natural attenuation, and that can limit acid production and metal-mobilization in reactive mineral tailings, have been proposed and demonstrated at the laboratory scale. Active biological remediation systems allow metals to be recovered and recycled, rather than to be disposed of in mixed-metal sludges (from active chemical treatment), or in spent composts (from mine water passive treatment). Using empirical engineering, microbiological systems can be used to selectively capture (by bio-mineralization) individual metals from mine process waters and acid mine drainage. Capturing and recycling metals from mine waters also avoids the necessity of storing metal-rich sludges and composts produced in current remediation approaches, which have the inherent risk of remobilization of metals and further contamination of the environment.

Conflicts of Interest

The author declares no conflict of interest.

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