Evolution of Acid Mine Drainage Formation in Sulphidic Mine Tailings

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Abstract: Sulphidic mine tailings are among the largest mining wastes on Earth and are prone to produce acid mine drainage (AMD). The formation of AMD is a sequence of complex biogeochemical and mineral dissolution processes. It can be classified in three main steps occurring from the operational phase of a tailings impoundment until the final appearance of AMD after operations ceased: (1) During the operational phase of a tailings impoundment the pH-Eh regime is normally alkaline to neutral and reducing (water-saturated). Associated environmental problems include the presence of high sulphate concentrations due to dissolution of gypsum-anhydrite, and/or effluents enriched in elements such as Mo and As, which desorbed from primary ferric hydroxides during the alkaline flotation process. (2) Once mining-related operations of the tailings impoundment has ceased, sulphide oxidation starts, resulting in the formation of an acidic oxidation zone and a ferrous iron-rich plume below the oxidation front, that re-oxidises once it surfaces, producing the first visible sign of AMD, i.e., the precipitation of ferrihydrite and concomitant acidification. (3) Consumption of the (reactive) neutralization potential of the gangue minerals and subsequent outflow of acidic, heavy metal-rich leachates from the tailings is the final step in the evolution of an AMD system. The formation of multi-colour efflorescent salts can be a visible sign of this stage.

Keywords: mining; metal; tailings; oxidation; acid mine drainage; waste management; pollution; solubility; reductive dissolution; sulphide; ore deposit; sustainability
1. Introduction

Mine tailings are among the largest mining wastes on Earth and can reach surface areas of up to 52 km² [1] and be several hundred meters high. As this waste type results mainly from the flotation process of sulphide mineral ores they are very likely to produce acid mine drainage (AMD), the main environmental problem of contemporary mining activity. The on-land deposition has many environmental, socio-economic, and geotechnical stability problems, which can make them a limiting factor to production in the mining industry. Tailings require large land areas and they have a great potential to produce ground and surface water contamination due to mineral dissolution in the operative and post-operative stage. Leaching from tailings results in an increase of oxyanions in solution (e.g., sulphate, arsenate, molybdate) during operation, and AMD formation after operation. Additionally it also represents a threat downstream in case of catastrophic dam failures, as has happened in the past [2]. The public becomes concerned and the mining operations have to compete with alternative land uses like agriculture, fisheries, or tourism. As a result, the mining industry is re-evaluating the option of submarine tailings disposal (STD), a heavily disputed practice used in some locations over the last few decades primarily resulting in negative impacts on the environment (reviewed in an other paper of this special issue on submarine tailings disposal (STD) [3]).

This review summarizes the work of 20 years of research on AMD in order to understand the evolution and the controlling parameters of AMD formation in this type of mine waste.

The review starts with an introduction into the biogeochemical processes occurring during sulphide oxidation and then focuses on the very beginning of the process in the transport channels of the tailings onto the tailings impoundments and the processes occurring in active operations. Then follows the evolution of AMD formation after the operation of the tailings impoundment has ceased, in relation to time, climate, deposition technique and flotation and finally ore deposit type will be analyzed. The biogeochemical processes involved are highlighted in multi-extreme environments. At the end of this review, problems of management, remediation, and prevention options are discussed in order to increase the sustainability of mining operations.

For this purpose, we use mainly studies from porphyry copper ore deposits as examples, but this knowledge on the mineralogy and the resulting geochemistry can be extended with due caution to other sulphide ore deposits. Terminology and technical descriptions in this article have been kept simple so as to provide a review that can be used by a wide audience. For more details please refer to the specific research articles.

2. Sulphide Oxidation

For the proper understanding of the formation of acid mine drainage, the biogeochemical interactions and the sequences in these processes have to be understood. This chapter is taken from Dold [4] for the convenience of the reader and more details on this issue can be found in this open access book chapter free of charge.

The problem of sulphide oxidation and the associated generation of acid mine drainage (AMD), or more generally acid rock drainage (ARD), as well as the dissolution and precipitation processes of metals and minerals, has been a major focus of investigation over the last 50 years [5–9]. The primary
Mineralogical composition has a strong influence on the oxidation processes. This has been well illustrated [10–12], showing that reaction rates display significant differences depending on which sulphides are being oxidized by Fe(III) and the potential Fe(III) hydroxide coating. Kinetic-type weathering experiments indicate the importance of trace element composition in the stability of individual sulphides. Where different sulphides are in contact with each other, electrochemical processes are likely to occur and influence the reactivity of sulphides [13].

Most mines are surrounded by piles, dumps, or impoundments containing pulverized material or waste from the benefaction process (Figure 1A), which are known as tailings, waste rock dumps, stockpiles, or leach dumps or pads. Waste rock dumps generally contain material with low ore grade, which is mined but not milled (Run of Mine; ROM). These materials can still contain large concentrations of sulphide minerals, which may undergo oxidation, producing a major source of metal and acid contamination [14]. In the following section the focus is on the acid producing sulphide minerals, mainly using pyrite as an example.

The most common sulphide mineral is pyrite (FeS2). Oxidation of pyrite takes place in several steps including the formation of the meta-stable secondary products ferrihydrite (5Fe2O3·9H2O), schwertmannite (between Fe8O8(OH)6SO4 and Fe16O16(OH)10(SO4)3), and goethite (FeO(OH)), as well the more stable secondary jarosite (KFe3(SO4)2(OH)6), and hematite (Fe2O3) depending on the geochemical conditions [6,9,11,15–18]. Oxidation of pyrite may be considered to take place in three major steps: (1) oxidation of sulphur (Equation (1)); (2) oxidation of ferrous iron (Equation (2)); and (3) hydrolysis and precipitation of ferric complexes and minerals (Equation (4)). The kinetics of each reaction is different and depends on the conditions prevalent in the tailings:

\[
\text{FeS}_2 + \frac{7}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad (1)
\]

\[
\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O} \quad (2)
\]

Equation (1) describes the initial step of pyrite oxidation in the presence of atmospheric oxygen. The oxidation of ferrous iron to ferric iron, is strongly accelerated at low pH conditions by microbiological activity (Equation (2)), producing ferric iron as the primary oxidant of pyrite (Equation (3)) [7,19,20]. Under abiotic conditions the rate of oxidation of pyrite by ferric iron is controlled by the rate of oxidation of ferrous iron, which decreases rapidly with decreasing pH. Below about pH 3 the oxidation of pyrite by ferric iron is about ten to a hundred times faster than by oxygen [21].

It has been known for more than 50 years that microorganisms like Acidithiobacillus ferrooxidans or Leptospirillum ferrooxidans obtain energy by oxidizing Fe2+ to Fe3+ from sulphides by catalyzing this reaction [22] and this may increase the rate of Reaction (2) up to the factor of about 100 over abiotic oxidation [23]. More recent results show that a complex microbial community is responsible for sulphide oxidation [19,24–27]. Nordstrom and Southam [28] stated that the initiating step of pyrite oxidation does not require an elaborated sequence of different geochemical reactions that dominate at different pH ranges. Acidithiobacillus spp. forms nano-environments, which grow on sulphide mineral
surfaces [29]. These nano-environments can develop thin layers of acidic water that do not affect the bulk pH of the water chemistry. With progressive oxidation, the nano-environments may change to microenvironments [30]. Evidence of acidic microenvironments in the presence of near neutral pH for the bulk water can be inferred from the presence of jarosite (this mineral forms at pH around 2) in certain soil horizons where the current water pH is neutral [31]. Barker et al. [32] observed microbial colonization of biotite and measured pH in microenvironments in the surroundings of living microcolonies. The solution pH decreased from near neutral at the mineral surface to pH 3–4 around micro-colonies living within confined spaces at interior colonized cleavage planes.

Figure 1. (A) Open pit mine surrounded by waste dumps and stock-piles. (B) Semi-Autogenous Grinding (SAG) mill. (C) Froth flotation of chalcopyrite concentrate. (D) Deposition point of a tailings impoundment. (E) Areal photograph of a valley dam tailings impoundment. Note the slight saturation of the tailings and the seepage in the dam (dark humid spots in the dam). And (F) areal view of a big tailings impoundment with near complete water saturation.
When mine water, rich in ferrous and ferric iron, reaches the surface it will fully oxidize and hydrolyze, resulting in the precipitation of ferrihydrite (Fh), schwertmannite (Sh), goethite (Gt), or jarosite (Jt) depending on the pH-Eh conditions, and availability of key elements such as potassium and sulphate (Figure 2). These secondary minerals like jarosite, schwertmannite and ferrihydrite are meta-stable and can transform into goethite [17].

The hydrolysis and precipitation of iron hydroxides (and to a lesser degree, jarosite) will produce most of the acid in this process. If the pH is less than about 2, ferric hydrol ysis products like Fe(OH)$_3$ are not stable and Fe$^{3+}$ remains in solution:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \quad (4)$$

Note that the net reaction of complete oxidation of pyrite, hydrolysis of Fe$^{3+}$ and precipitation of iron hydroxide (sum of Reactions (1), (2) and (4)) produces four moles of H$^+$ per mole of pyrite (in case of Fe(OH)$_3$ formation, see Reaction (5), i.e., pyrite oxidation is the most efficient producer of acid among the common sulphide minerals (net Reaction (5)). Nevertheless, it is important to be aware that the hydrolysis of Fe(OH)$_3$ is the main acid producer ($3/4$ of the moles of H$^+$ per mol pyrite).

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad (5)$$

The process of pyrite oxidation relates to all sulphide minerals once exposed to oxidizing conditions (e.g., chalcopyrite, bornite, molybdenite, arsenopyrite, enargite, galena, and sphalerite among others). In this process different amounts of protons are released [4] and the metals and other harmful elements or compounds are released to the environment.

3. From the Flotation Process to the Active Tailings Impoundment

The goal of the flotation process is to separate the economically valuable target minerals from the gangue minerals, which have no economic value at the time of exploitation [33]. In order to be able to do this, the rocks extracted from the mine (underground or open pit) as coarse ROM granulometry (including blocks of 1 m diameter down to rock powder), have to be broken, ground and milled (Figure 1B) to a very fine grain size, in order to be able to separate on the addition of chemical reagents, selectively the target minerals (i.e., to make it hydrophobic, which then enables it to attach to introduced air bubbles and so float towards the surface of the flotation cell (Figure 1C), were it can be harvested) [34,35]. Non-economic sulphide minerals, like pyrite can be suppressed from flotation as for example by pH adjustment (alkaline circuit), and end up in the waste materials, which are called tailings (Figure 1D). As the flotation process has a recovery of 80%–90%, between 10% and 20% of the target mineral ends up in the tailings together with the non-economic sulphides like pyrite or other accessory sulphides, which can contain other environmentally harmful elements. These tailings are then sent in suspension via tubes, channels or directly in riverbeds towards their final disposal sites (Figure 1D), i.e., a river, lake(s), or the sea, but mainly in mines today on-land in constructed, tailings impoundments or dams (Figure 1E,F). Depending on the geochemical conditions of this final disposal site, the mineral assemblage in the tailings can undergo geochemical oxidative processes, which can lead to the release of metals, toxic compounds, and acid. The geochemical and mineralogical effects of disposal of mine tailings in reducing environments is reviewed in another paper of this special issue.
concerning submarine tailings disposal (STD) [3]. The present review focuses on the processes resulting from the exposition of sulphidic mine tailings to oxidation in on-land tailings impoundments.

The whole flotation process is performed using a mineral suspension with a solids-water ratio of about 40%:60%. Thus, the flotation is a highly water consuming process, and therefore water is the limiting factor for mine development in many arid to semi-arid regions (e.g., Northern Chile and Southern Peru). Some mining operations have opted to use marine water for the flotation process [36,37]. Water recycling from the decantation pond of the tailings impoundment is also a common practice to recover industrial water. New techniques like paste tailings and dry staking recover water before final deposition and increase geotechnical safety of the tailings deposit [38,39]. However, it should be noted that sulphide oxidation is enhanced by these new techniques, as the tailings are never completely water saturated, but humid, and oxygen can more easily reach the sulphides, compared to the traditional water-saturated tailings impoundments.

In the flotation process, tailings come in to contact with water and oxygen for the first time, leading to Reaction (1). However, at this stage the oxygen supply is limited, as only dissolved oxygen is available for the sulphide oxidation in the flotation process. As most flotation processes are maintained artificially at alkaline pH conditions in order to suppress the flotation of pyrite, sulphide oxidation during the flotation does not result in extensive acid generation. However, isotopic studies (\(\delta^{34}S, \delta^{18}O\)) of dissolved sulphate suggest along a 87 km long tailings channel that sulphide oxidation starts in the flotation process and during transport towards the final disposal site [40]. Additionally, if the ore has oxyanions associated with iron oxide minerals, for example when ore is slightly pre-oxidized by supergene processes in the upper part of the ore deposit, then, due to the alkaline flotation circuit, As and Mo can be desorbed during flotation and possible make it necessary to implement an abatement plant for these elements, as is the case for Mo in the El Teniente mine, Chile.

When the tailings reach the active tailings impoundment, they should then in a strict sense be maintained water saturated in order to minimize oxidation of the sulphide minerals (water contains a maximum of approximately 10 mg/L dissolved oxygen). This is not always the case or possible, for example due to high evaporation rates in dry climates, so that often parts of the tailings are exposed during summer time to a thin unsaturated zone to oxidation even in active tailings impoundments (Figure 1E). At this stage, the 21% of atmospheric oxygen will start to oxidize the sulphide mineral assemblage present in the tailings. This goes hand-in-hand with the increase of pore water concentration in metals and oxyanions like (Na, K, Cl, SO\(_4\), Mg, Cu, Mo) towards the surface due to capillary transport, and the formation of efflorescent salts on the surface, like halite, gypsum, and Na-K-Ca-Mg sulphates like mirabilite Na\(_2\)SO\(_4\)#10H\(_2\)O and syngenite K\(_2\)Ca(SO\(_4\))#4H\(_2\)O) [1,40]. Due to neutral to alkaline pH at this stage, only major cations together with sulphate and chloride are mobile and the resulting efflorescent salts are mainly white in colour.

Another commonly observed geochemical process occurring in active tailings of porphyry copper deposits is a strong increase in sulphate concentrations, which typically range between 1500 and 2000 mg/L, with an annual trend to increase towards the end of summer (Figure 2) and sometimes a general increase with time can also be observed. The sulphate concentrations are controlled by the solubility of gypsum [40,41], often present in an ore deposit (gypsum or anhydrite), and the increase by the release of sulphate due to weathering processes associated with sulphide oxidation. Neutralization reactions, e.g., silicate weathering, liberates major cations into solution, which then form sulphate
complexes, so that higher concentrations of sulphate can stay in solution, than can be explained by the solubility of gypsum alone.

**Figure 2.** Example of the evolution of dissolved sulphate concentrations (in mg/L) in the decantation pond of an active tailings impoundment during a five year period. A clear seasonal trend is observed, peaking end of summer due to evaporation effects.

In some tailings impoundments the formation of AMD can be visualized during the operational phase in the dam area [42,43]. This is mainly the case when the dam is made of the coarser fraction of the tailings (e.g., hydro-cyclone separation). This results in a higher content of sulphide minerals in the dam material, which has also a coarser grain size (sandy material). Additionally, the dam must be maintained in an unsaturated condition for stability reasons, so that this area is an excellent environment for sulphide oxidation, which is visible by the precipitation of schwertmannite from the effluents at the foot of the dam [42,43]. The presence of schwertmannite directly at the outcrop of the tailings dam, suggests that acidic (pH 2–4) and ferric iron rich solutions are leaching from the tailings. If a ferrous iron rich neutral plume flows out from the dam, then iron oxidation will occur followed by hydrolysis and subsequent ferrihydrite precipitation [43]. If the ferrous iron rich plume is acidic, then temperature, pH, and microbiological activity will determine how fast the ferrous iron will be oxidized in the drainage stream [44,45] in order to be able to subsequently hydrolyze and precipitate as lepidocrocite, schwertmannite, jarosite or ferrihydrite, depending on the final geochemical conditions.

In general, it can be pointed out, that if an active tailings impoundment shows signs of acidification in the decantation pond during operation or even of AMD formation, then severe management problems can be assumed.

Summarizing, active tailings impoundments might have the following environmental problems:

1. Increased sulphate concentrations (between 1500 and 2000 mg/L), if gypsum and/or anhydrite are present in the ore mineralogy (e.g., porphyry coppers). The sulphate concentrations are controlled by the gypsum equilibrium. The sulphate concentrations can additionally increase with time in the tailings impoundment, depending on increasing input of major cations from weathering processes.

2. If oxyanions (e.g., arsenate, molybdate) are associated with Fe(III) hydroxides from the primary ore mineralogy, they will potentially be released in the alkaline flotation process.
3. During the flotation process and tailings transport, sulphide oxidation can begin, but will not be able to strongly influence the geochemical regime (i.e., the pH will not drop dramatically). In the active tailings impoundment, when a thin, unsaturated zone develops in the dry season, then sulphide oxidation can lower pH conditions and increase the metal release in the uppermost part of the tailings.

4. In situations where tailings dams are constructed by coarse tailings material, sulphide oxidation might lead to the release of AMD from the unsaturated dam area. This might be visible by the precipitation of schwertmannite and/or ferrihydrite [42,43].

5. The precipitation of these Fe(III) hydroxides in the pore space of the tailings dam might change the permeability and so produce stability problems for the tailings dam.

4. Evolution of Post-Deposition Geochemical Processes in Tailings Impoundments

In order to study the evolution of sulphide oxidation in a natural environment after the operation has ceased, the Talabre tailings impoundment of the Chuquicamata porphyry copper mine was investigated [1]. Although the Talabre tailings impoundment is an active impoundment, its dimensions (52 km² surface area) and deposition technique allowed a study of tailings exposure at a well defined time frame under the hyper-arid conditions of the Atacama Desert. As the deposition point is periodically changed on the tailings surface of the impoundment and the tailings are disposed of into different basins, there was an exact register available of how long the tailings were exposed to the atmosphere, i.e., weathering. This gave the possibility to select the samples sites from fresh tailings (actual discharge point at time of sampling) up to five years of exposure and track the mineralogical and geochemical changes over time. The mineralogy of the tailings is typical of porphyry copper systems, with pyrite as the major sulphide (1.75 wt %), followed by chalcopyrite and bornite. Minor sulphide fractions found in polished sections were enargite, covellite, chalcocite and sphalerite. There were no carbonates present in the mineral assemblage and the gangue mineralogy was dominated by quartz, K-feldspar, plagioclase, biotite, chlorite, muscovite and gypsum. Primary anhydrite was not found due to hydration to gypsum during flotation. Apatite, rutile, magnetite, hematite, and goethite occurred in trace amounts [1].

The key parameters, pH and Eh, evolved from alkaline (fresh tailings pH 9.1) towards acidic and from reducing to oxidizing conditions. After three years of oxidation the pH was still in the circumneutral range (pH 6.4–7.5), while after four years a drop to acidic conditions was observed (pH 4.7) at the surface (0–4 cm), leading to a pH of 3.9 after five years with the development of a well defined 29 cm thick oxidation zone (Figure 3A).

Associated with this geochemical change, the main element groups in this system showed their characteristic behaviour and distribution. The major cations and anions showed an increasing trend of enrichment towards the tailings surface, due to capillary transport in the hyper-arid climate [1,46–48], with the fast precipitation of halite, gypsum, and Na-K-Mg-Ca sulphates and chlorides at the surface (mainly white efflorescent salts). Heavy metal cations like Cu, Zn, and Ni were not mobile in the neutral to alkaline pH conditions in the first years due to their sorption behaviour to iron oxides. However, after five years of oxidation, the drop of the pH in the oxidation zone resulted in increasingly high concentrations of Cu (up to 170 mg/L) and Zn (150 mg/L) in the pore water near the surface of the tailings. This was visible by the precipitation of greenish eriochalcite (CuCl₂·2H₂O) on
the tailings surface, as observed in other chloride-rich environments [47,48]. In contrast, arsenic and molybdenate, which are stable as oxyanions in solution, occurred in high concentrations in the pore water due to the alkaline conditions at the beginning of weathering. The origin of these elements is mainly due to high natural background concentrations of As in the area [49], desorption of oxyanions associated with Fe(III) hydroxides in the ore mineralogy, and increasing concentrations in the recycled industrial water due to evaporation. With decreasing pH by sulphide oxidation and hydrolysis of Fe(III) hydroxides in the oxidation zone, arsenate and molybdenate decrease their concentrations in the pore water of the oxidation zone to below detection limits due to the well known adsorption to the neo-formed sorbents (Fe(III) hydroxides). This is confirmed by sequential extraction data, showing a strong increase of As (175 mg/kg) and Mo (155 mg/kg) associated with the Fe(III) hydroxide fraction in the upper oxidation zone after five years of oxidation. Stable isotope data also clearly demonstrated that sulphate had its origin at the beginning from gypsum dissolution, while in the acid oxidation zone a clear change towards the supply of sulphate by sulphide oxidation is observed [1].

**Figure 3.** (A) Oxidation zone in the Talabre tailings impoundment after five years of oxidation (pH 3.9). Clearly visible the precipitation of Fe(III) hydroxides and the oxidation front [1]. (B) Precipitation of ferrihydrite in an active tailings impoundment due to the exposure of Fe(II)-rich waters to the atmosphere (Ocroyoc, Cerro de Pasco, Peru) [14]. And (C) outcrop of AMD (pH 3.15) at the foot of an active tailings dam with the precipitation of schwertmannite (Ojancos, Hochschild, Chile) [42].

These findings explain why standard kinetic cell tests for AMD prediction (ASTM D5744-96) [50] do not correctly predict the behaviour of porphyry copper material [51,52]. As seen in the case of Talabre, the material needs at least 3–4 years in order to reach acidic pH conditions, and this without any buffering from carbonates. Therefore, the time frame proposed in the standard method of 25 cycles (half year or up to one year depending on the length of each cycle), is far too short in order to reach, *i.e.*, predict, acidic conditions in the porphyry copper system. While there is some improvement, *i.e.*, increased oxidation kinetics with new modified cell tests [53,54], they still have to be run for at least 2–3 years, until acid conditions are reached (in case the acid base accounting indicates an excess of acid potential; the usual case for porphyry copper deposits [46]). This increases the costs and time scale for mine waste characterization, which is not very attractive for the mining industry.

In the study of the Talabre tailings impoundment, another important process for tailings management could be observed. As the tailings deposition point returns periodically to the same place of deposition, where the tailings were exposed to oxidation over several years with the subsequent formation of the
above described oxidation zone and formation of efflorescent salts on the surface, this re-deposition will have the following geochemical impact: As explained before, after 4–5 years a well defined acid oxidation zone has developed with the formation of secondary Fe(III) hydroxides (Figure 3A), which have the role of the sorbent for arsenic and molybdenum in these geochemical condition. With the new deposition of fresh alkaline tailings in the same place were the acid oxidation zone formed in an unsaturated zone of the tailings stratigraphy, the system is changed to saturated, alkaline reducing conditions. This will first dissolve all efflorescent salts and liberate the associated elements into the aqueous phase, but also it will initiate the reductive dissolution of Fe(III) hydroxides from the oxidation zone, which will liberate the associated As (up to 23 mg/L) and Mo (up to 16 mg/L) to the groundwater of the tailings impoundment [1].

5. Biogeochemical Iron Cycling at the Oxidation Front: The First Step in the Formation of Acid Mine Drainage (AMD)

Until now we have observed how the system evolves over time at the surface and its element-release sequence. In this section we will enter in more detail into the biogeochemical interactions occurring at the oxidation front and in the vertical stratigraphy, in oxidation zones that are well developed.

This is the case (for example), after 16 years of oxidation in the high mountain climate Piuquenes tailings impoundment, Chile [46,55–58]. Its oxidation zone reached pH 2.3–3 and nearly all sulphide minerals were oxidized (Eh = 750 mV), only some relicts of pyrite and chalcopyrite remained (Figure 4). The secondary mineral assemblage was controlled by schwertmannite, jarosite, gypsum, and a vermiculite-type mixed layer mineral resulting from the alteration of biotite in the oxidation zone [46]. Below the oxidation front, a change from acidic-oxidizing conditions towards more reducing (500 mV, which is controlled by the Fe\(^{3+}/Fe^{2+}\) redox pair) and an increase to pH 4.5 (Gibbsite buffer) can be observed [55] (Figure 4B). Iron speciation in the pore water was dominated by ferric iron in the oxidation zone (up to 2000 mg/L), while directly below the oxidation front a ferrous iron plume of up to 4000 mg/L could be detected [55].

The above-mentioned increase of pH at the oxidation front should initiate the hydrolysis of the Fe\(^{3+}\) ions and the precipitation of Fe(III) hydroxides in this area of the profile. However, data from sequential extractions show the contrary, that at the oxidation front and below there were less secondary Fe(III) hydroxides precipitated than in the oxidation zone itself and the underlying primary zone [55]. This can be explained as follows (Figure 4A): At the oxidation front, main microbial activity was detected by Diaby et al. [57], due to the fact that sulphides are still available as energy source (in the oxidation zone they are mainly consumed and only ferric iron is available). In this study, the authors also found that Leptospirillum spp. are dominating the system and that the bacterial population was about 100 times greater at the oxidation front than above or below this horizon. However, Acidithiobacillus spp. and Acidiphillum spp. were also detected and seemed to be mainly responsible for iron reduction in this system, as Leptospirillum spp. is only able to oxidize ferrous to ferric iron. The \(\delta^{18}O\) values of dissolved sulphate suggest that from the top of the oxidation zone downwards to the oxidation front, a change from initially atmospheric oxygen towards oxygen from water can be observed. This indicates that at the oxidation front sulphide oxidation takes place by ferric iron, while towards the tailings surface more atmospheric oxygen is involved [56].
Sulphate reducing bacteria were also detected, and found to have their highest number below the oxidation front, so that some sulphate reduction can be expected. However, stable isotopic data suggest that due to the lack of increase of $\delta^{34}$S shift towards heavier signature in this area of the profile, sulphate reduction is not occurring in a significant amount in this system, possibly due to the limited availability of organic matter. In the oxidation zone, no organic molecules like low molecular weight carboxylic acids (LMWCA) could be detected, so that the only organic matter is possibly dead bacteria cells available for organic carbon cycling. In contrast, below the oxidation front a peak of LMWCA, like acetate, formate, and pyruvate could be detected. Associated with this LMWCA peak, which is interpreted to be a result of the microbial activity around the oxidation front, the ferrous iron plume and an increase in CO$_2$ in the pore gas correlates directly [55,60]. These data suggest that the microbial community, in this case mainly *Acidithiobacillus ferrooxidans* and/or *Acidiphilium* spp. [61] use the monodentate LMWCA like acetate and formate as electron donors and ferric iron as electron sink, resulting in the reduction to ferrous iron and the formation of CO$_2$ [55]. This reduction increases the mobility of iron, as now the ferrous iron can migrate in the circumneutral pH conditions of the underlying tailings stratigraphy until it outcrops at the foot of the dam, where it will auto-oxidize and hydrolyze to form ferrihydrite (outcrop pH still neutral). Another process, which might enable the ferric iron to pass the geochemical barrier of the oxidation front, is via complexation by bidentate LMWCA like oxalate or pyruvate, which changes the solubility and therefore, these complexes might...
reach a lower tailings horizon, where then again the microbial community will reduce it to ferrous iron and CO$_2$. Thus, these processes explain why at and below the oxidation front less secondary Fe(III) hydroxides precipitate and instead a ferrous iron plume is formed due to iron reduction processes. This plume can now migrate in the system until it encounters more oxidizing condition or higher pH conditions (e.g., in contact with carbonate rich strata, which then promote the hydrolysis of ferrihydrite). This will be the first visible indication of AMD formation, although the main flow path in the tailings is still neutral (Figure 3B).

The change in redox at the oxidation front also triggers the replacement of chalcopyrite with covellite by copper, leached out from the overlying oxidation zone downwards (Figure 4B), due to general downwards-dominated movement of the released elements in the rainfall dominated alpine climate of Piuquenes [46]. The thickness of this copper enrichment is limited by a second pH increase towards pH around 5.5–6 (siderite buffer) at 3 m depth, as Cu is only mobile until pH 5 in freshwater and is therefore adsorbed at higher pH conditions [46]. As the oxidation front is defined by the drop of oxygen concentrations to zero in the pore gas of the tailings profile (70 cm depth), which correlates with a pH and redox switch, and the groundwater level was at 4 m depth, the copper enrichment zone is defined between oxidation front and siderite buffer (0.7–3 m depth) [55]. This means, that the general belief that supergene enrichment is associated with the groundwater level is not necessarily correct. It is defined by the oxidation front and the pH gradient induced by the neutralization reactions of the gangue mineralogy, which controls the thickness of the mobility window of copper (pH < 5 and Eh < 500 mV), necessary for the enrichment process. This is the case in fresh water systems, but in high-chlorine system Cu can be mobile at neutral pH as Cu(II)Cl$_2$ or Cu(I)Cl$_2$ complexes [47].

### 6. Consumption of the Neutralization Potential and Final Acid Flow

As discussed above, the resulting ferrous iron plume is the first sign of AMD that might outcrop. However the production of protons still goes on at the oxidation front and in the oxidation zone. These protons interact with the gangue mineralogy and will be partly neutralized, liberating other elements into solution from the dissolution processes of carbonates and silicates. Therefore, depending on the composition of the mineral assemblage of the gangue mineralogy a specific neutralization sequence can be observed across the tailings stratigraphy, which is controlled by the different buffering minerals. For example, in the Piuquenes tailings impoundment the carbonates present are dominated by siderite with traces of calcite. Thus, when the protons produced by sulphide oxidation migrate with the acid solution downwards, first calcite will buffer to around neutral pH until it is completely consumed or passivated by iron oxides. Then siderite will buffer the system to around pH 5.5, until it is consumed. Then the pH can drop further down to around pH 4.5, were the gibbsite buffer will maintain the pH until also this buffer is consumed. Finally, in the oxidation zone itself, the Fe(III) hydroxide assemblage will buffer the pH around the typical pH between 2 and 3 in this area. If it is close to pH 2 a dominance of jarosite can be expected, while if it is closer to pH 3 schwertmannite will control the system [4,46,55]. If there is still an excess of protons added to the system, in some cases even the jarosite buffer might be consumed and even negative pH can be reached as reported from Iron Mountain [62].

This sequence of pH values increases from 2–3, to 4.5, 5.5 and neutral correlates with a successive decrease in redox potential occurring in oxidised tailings, clearly defining the geochemical systems.
active in each zone, and controlling which elements can be mobilized downwards through the tailings stratigraphy.

Oxyanions like arsenate and molybdate are retained effectively by the Fe(III) hydroxides due to sorption at low pH conditions in the oxidation zone. Below, due to reduction of arsenate to arsenite or at very low pH condition arsenate will be completely protonized and therefore the mobility might be increased for arsenic under these specific conditions [63].

Heavy metals occur mainly as divalent cations, stable in solution and mobile at low-pH conditions. With increasing pH, they become adsorbed and therefore immobile [4]. Additionally, as observed above in the case of copper, replacement processes and reduction processes can precipitate the metals as secondary sulphides or hydroxides in a deeper part of the stratigraphy [46]. As the system will increasingly acidify, these secondary sulphides will be re-dissolved and so the acid oxidation zone migrates further down, increasing the mobility of the heavy metals. When the protons produced in the oxidation zone exceed the neutralization capacity of the gangue mineralogy below in the tailings stratigraphy, the situation can be reached where the whole flow path is under acid conditions, so that the acid, heavy metal rich solution can outcrop at the foot of the tailings dam, or infiltrate into the groundwater. This will be visible with a broad range of bright colours of the precipitates forming at the outcrop, as secondary heavy metal sulphate minerals can have blue, yellow, green, or red colours, depending on their composition (Figure 5). Therefore, when you observe bright colours at the foot of your tailings dam, you can expect an advanced system with acid flow path, or you have an active tailings dam built using the coarse tailings fraction and you are observing the effect of the sulphide oxidation in the unsaturated dam.

Figure 5. Acid flow precipitates: (A) Efflorescent salts surface of acid oxidation zone pH 2.5, Ite Bay, Peru. (B) Efflorescent salts at the Excelsior Waste rock dump, Cerro de Pasco, Peru. And (C) acid Effluent with chalcoalamite precipitation (light blue) at pH 4.9 and schwertmannite at pH 3.15 (orange-brown) at Ojancos, Copiapó, Chile.

7. Some Common Errors in AMD and Mine Waste Management

7.1. AMD Management → Fe³⁺-Rich Solutions

In mines, where AMD occurs, the Fe³⁺-rich solutions are sometimes pumped into the active mine tailings. This has to be avoided, as the input of ferric iron to sulphide rich material will efficiently oxidize the sulphides and produce 16 moles of protons per mole of pyrite oxidized (Equation (3)), with
the result that the pH might drop quickly in the active tailings impoundment [14]. Therefore, mine management strategies need to prevent the contact of the Fe$^{3+}$-rich solution with any sulphide containing material.

7.2. Fe$^{3+}$-Rich Sludge or Mud from AMD Neutralization or Treatment Plants

Lately, due to increased efforts in the mining industry not to dispose AMD to the environment, many mines have implemented AMD neutralization or treatment plants. This process produces a certain volume of sludge or mud, which is mainly ferricydrite, lepidocrocite, goethite [64], schwertmannite [65], depending on the process, with co-precipitated and/or adsorbed elements like arsenic, molybdenum or heavy metals. Thus, this sludge is now a hazardous waste material, which has to be managed properly. An often-used solution for its disposal and unfortunately performed in many mining operations is the deposition of iron oxide sludge in the active tailings impoundment.

The problem with this practice is highlighted here: The sludge of the treatment plant contains mainly Fe(III) hydroxides like ferrihydrite or schwertmannite, the two unstable Fe(III) hydroxides. If we dispose of this sludge together with the tailings from sulphide flotation, we add ferric iron to the sulphides and subsequently cover this sludge with more fresh tailings, so that they eventually end up in a reducing environment. Thus, the ferric iron from the sludge can oxidize the sulphides or undergo reductive dissolution; both processes will produce a ferrous iron plume (some times even acidic) in the tailings stratigraphy, which again will migrate down through the tailings stratigraphy of the active tailings impoundment. Therefore, even if we take (unrealistic) precautions to prevent sulphidic tailings from coming in contact with the atmosphere, e.g., by maintaining a water saturated tailings impoundment, so that only minimum sulphide oxidation can occur, and we cover the tailings directly after the operation has ceased to prevent any further oxidation, the tailings impoundment will one day produce AMD, when the ferrous plume formed due to the addition of the ferric sludge flows out from the foot of the tailings dam.

With these examples we have learned, that we should not mix mine waste from different geochemical systems. Do not mix sulphides with Fe(III) hydroxide sludge in a tailings impoundment, or you will increase the volume of the waste and create adverse geochemical reactions, increasing your long-term environmental management costs. The same is the case for hazardous materials, containing problem elements in the form of oxyanions (e.g., As, Mo, Cr, SO$_4$), as they should not be mixed with material that contains heavy metals (e.g., Cu, Zn, Ni, Cd, Pb) due to the reverse sorption behaviour. Confine your reactive waste separately in well-designed disposal facilities, so that the geochemical reactions can be controlled long-term and no hazardous elements can escape these systems to the hydrological system surrounding your operations. This will also help future generations to re-exploit these resources with better techniques than are available today.

8. Conclusions

Sulphide oxidation and the subsequent formation of acid mine drainage (AMD) in mine tailings impoundments is associated with a sequence of biogeochemical and mineral dissolution processes and can be classified in three main phases from the operational phase towards the final outcrop of AMD.
8.1. Operational Phase of a Tailings Impoundment: Neutral-Alkaline Oxyanions-Rich Effluents (Figure 6A)

During the operational phase of a sulphidic mine tailings impoundment, no sulphide oxidation should occur, when it is properly managed. This means it should be completely water saturated without exposure of the tailings to the atmosphere, and the system should maintain neutral to alkaline pH conditions (Figure 6A). If this is not the case, sulphide oxidation might start in the unsaturated parts of the tailings, as well as in the tailings dam, if it is built with the coarser fraction of the tailings themselves. This might lead to sulphide oxidation and AMD formation during the operational phase. In ore deposit types, which contain soluble sulphate minerals like gypsum-anhydrite (e.g., porphyry copper deposits), high $SO_4$ concentrations can be expected in the tailings controlled by the solubility of these minerals, with a typical range between 1500 and 2000 mg/L $SO_4$.

Additionally, if the ore deposit shows some pre-oxidation naturally or due to the exploitation process, such as block-caving, elements like arsenic or molybdenum, which are adsorbed onto Fe(III)hydroxides, might be desorbed in the alkaline flotation circuit and maintain elevated concentrations in the active tailings impoundment and its effluents. These processes might lead to the need for implementation of sulphate treatment plants or a facility for Mo treatment as in the case of the Carén tailings impoundment from the El Teniente mine, Chile. Mine tailings should not be used as a general waste dump for other industrial waste material, as this might produce severe environmental risks for the whole system and importantly might increase the environmental waste management costs. The visible signs of this stage are usually white precipitates on the surface or around leachates (at this stage the patient is starting to feel bad and have some problems, he becomes pale, but there is still time for prevention).

8.2. After Operation Ceases; Neutral Ferrous Plume Outcrop (Figure 6B)

When the active operational phase ceases, no water and tailings are deposited, which will lead to a drop in the groundwater level in the tailings impoundment and produce an unsaturated zone, where atmospheric oxygen can start the process of sulphide oxidation. This will lead over several years to the formation of an acid oxidation zone, where heavy metals leach out and oxyanions like As and Mo are adsorbed onto the secondary Fe(III) hydroxides formed due to sulphide oxidation. Additionally, due to reduction processes at the oxidation front a ferrous iron plume is formed in the stratigraphy of the tailings impoundment. This ferrous plume can then migrate through the still neutral stratigraphy downwards through the tailings. Once this ferrous plume (which might contain high sulphate concentrations and other oxyanions like As and Mo in solution) outcrops at the foot of the dam for example, the ferrous iron will auto-oxidize due to the neutral pH and precipitate as ferrihydrite (Bordeaux red). This outcrop of the neutral ferrous plume is the first visible sign of the AMD formation process. With subsequent hydrolysis producing ferrihydrite, the effluent will be acidified and the final pH will depend on the buffering capacity of the effluent.

Now the patient has still increased blood pressure (visible red head) and needs help, for prevention it might be too late, most likely long-term treatment is needed. Only by drillings and piezometers can this stage be detected in the tailings stratigraphy in time (it is like taking the blood pressure, if there is no visible sign).
Figure 6. The here shown tailings impoundment is a modern design, with integrated basement impermeabilization and internal drainage system. Most of the tailings impoundments around the world do not have impermeabilization and the contaminated solution will directly infiltrate into the groundwater. (A) During the operational phase the system is saturated and alkaline. There might be increased concentrations of oxyanions depending on the mineralogy of the ore. If the dam is built with the coarse fraction of the tailings, oxidation and acidification might start during the operational phase with first signs of AMD (Sh). Surface precipitates are white at this stage. (B) After operation has ceased, an acid oxidation zone will develop and a ferrous iron plume below the oxidation front can migrate at neutral pH conditions in the tailings stratigraphy. This neutral, ferrous iron-rich plume will produce ferrihydrite (Fh) at its outflow. And (C) acid production due to sulphide oxidation continues and the neutralization potential will be completely consumed, resulting in an acid flow in the tailings mobilizing heavy metal cations and resulting in the formation of AMD with multi-colour precipitates (mainly metal sulphates and/or chlorides).
If sulphide oxidation continues and the neutralization potential of the underlying gangue mineralogy is consumed, an acid flow will become established in the tailings. This enables heavy metals like Cu, Zn, Ni, Pb, and Cd to be mobilized through the tailings and outcrop at the foot of the dam or infiltrate into the groundwater, if no impermeable liners have been installed. The efflorescent salts resulting from this acid flow are brightly coloured, blue, green, yellow, white, or red depending on their elemental composition.

This is the final stage of AMD formation and the patient is now extremely ill (you can see it clearly in his green, yellow, blue face), where only final long-term treatment might mitigate the environmental damage. Prevention is here not possible any more, in some cases some drastic remediation with complete saturation of the system might help to alive the symptoms, if there is enough suitable water available [41,66] and the dam stability is not an issue.

Only proper studies can detect in time, at which stage an impoundment is present and predict how the evolution will continue. This is the key knowledge required in order to control and manage these systems properly long-term.

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Conflicts of Interest

The author declares no conflict of interest.

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