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Acid Mine Drainage in Chile: An Opportunity to Apply Bioremediation Technology

Johanna Obreque-Contreras, Danilo Pérez-Flores, Pamela Gutiérrez and Pamela Chávez-Crooker*
Aguamarina SA. Centro Tecnológico SR-97, Las Colonias 580, Antofagasta, Chile

Abstract

The use of micro organisms for heavy metal remediation in water is a technique widely studied. This review describes a number of methods used for acid mine drainage (AMD) remediation, containing high concentration of this type of contaminant. The AMD is a problem generated in abandoned mines and low grade stock of active mines, therefore it is an existing problem in mining countries. In this review it is described the problem in Chile, regulations and the challenge to resolved this problem for a sustainable industrial future.

Keywords: Acid mine drainage; Bioremediation; Chile

Abbreviation: AMD: Acid Mine Drainage

Introduction

The worldwide mining activities of ores are directly associated with acid mine drainage (AMD), which is recognized as one of the most serious environmental problems. Some effluents contain large quantities of toxic substances, such as cyanides and heavy metals, which have serious implications for human and ecological health. AMD is produced when sulfide-bearing material is exposed to oxygen and water.

Copper mining in Chile dates back at least three hundred years. At the beginning, extraction methods were simple because ores contained high grades of gold, silver, and copper. Over time as ore grade decreased, the extraction process has improved through the adoption of more sophisticated technology. At the present time, there is a high demand for treatments in order to recover AMD for further uses. However, the main concern will be focused on mine closure planning.

Many mining operations were abandoned in earlier years, prior to environmental regulations and without proper closure procedure. These abandoned operations are distributed throughout the country. Abandoned gold, copper, silver, poly-metal, carbon, and iron mines all represent significant risks to safety, human health and the environment. Further treatments are needed in order to finally close and recover these areas to give it back to the community.

The abiotic treatment technologies are highly efficient, but high costs due to the high-energy demand and large amounts of chemicals and expensive devices, then bioremediation appears as an attractive alternative; it is economically viable and environmentally friendly.

Bioremediation is an attractive and low cost operation to break down most of these contaminants through different mechanisms according with selected microorganisms, environment and final desired product. In this review we intend to introduce AMD, bioremediation techniques and the opportunity to apply them in the Chilean mining industry.

Acid Mine Drainage

Mining in Chile required great quantities of resources to work, due to the scale of their operations. A solution is to use a close circuit of solutions where every resource is used as much as possible with the positive consequence of reducing the waste production and controlling interactions between the process by-products and the environment [1]. Because acid generation and metals dissolution are the primary problems associated with pollution from mining activities. The chemistry of these processes appeared fairly straightforward, but gradually becomes complicated as geochemistry and physical characteristics can vary greatly from site to site [2].

The principal producer of acidic sulfur wastewaters is the mining industry. Water drainage in active, abandoned mines and mine tailings is often acidic (sometimes extremely so) [3]. Those acidic waters typically pose an additional risk to the environment by the fact that they often contain elevated concentrations of metals like iron, aluminum and manganese, and possibly other heavy metals and metalloid as arsenic, which is generally of greatest concern [3]. In the USA, the area polluted by AMD have been estimated, reaching 180,000 acres of lakes and natural reserves; 12,000 miles of rivers and channels. With an approximated cost of $32-72 billion dollars, while the Canada treating cost would be in the range $2-5 billion dollars [4].

AMD generation

The acidic mine drainage (AMD) is usually produced by the accelerated oxidation of iron pyrite, which is in fact the most common sulfide mineral worldwide [2,3,5].

Acid generations starts with Pyrite (FeS_2) and metals dissolution in coal and hard rock among others types of ore, which explains why AMD is a transversal issue for most of the copper sulfide, coal, and gold operations throughout the world. When pyrite is exposed to oxygen and water gets oxidizes, releasing hydrogen ion, acidity, sulfate ions, and soluble metal cations [2]. There is a bigger group of sulfide mineral which can be referred to as "pyrite type", as pyrrhotite, chalcopyrite, arsenopyrite, spharelite, galena and others that might initiate a similar processes leading to AMD production [5], turning this into a potentially catastrophic issue for countries as Chile, based on the typical mineralogy and the number of running and abandoned

***Corresponding author:** Pamela Chávez-Crooker, Aguamarina SA, Centro Tecnológico SR-97, Las Colonias 580, Antofagasta, Chile, Tel: +56-552892851; E-mail: pchavez@aguamarina.cl

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Mineral capable of producing AMD			
With oxygen		With ferric iron	
Mineral	Formula	Mineral	Formula
Pyrite	FeS_2	Spharelite	ZnS
Pyrrhotite	$Fe_{1-x}S$	Galena	PbS
Bornite	Cu_5FeS_4	Chalcopyrite	$CuFeS_2$
Arsenopyrite	FeAsS	Covelite	CuS
Enargite	Cu_3AsS_4	Cinnabar	HgS
Luzonite	Cu_3SbS_4		
Sulfarsenide	AsS	Millerite	NiS
Oropimente	As_2S_3	Pentlandite	$(Fe,Ni)_9S_8$
Stibnite	Sb_2S_3	Greenockite	CdS

Table 1: Minerals with AMD producing potential.

operations existing, especially on the north of the country, in case of south Brazil it has become the biggest environmental issue for the mining industry, especially at the south of Santa Catarina state and Rio Grande do Soul [4].

Table 1 shows different ores capable of producing AMD when exposed to oxygen or with ferric iron [1].

AMD is often characterized as low pH water with elevated concentrations of iron, sulfates and heavy metals, the heavy metals profile depend on the originating mineral deposit types [6]. Acid drainage is produced when minerals containing reduced forms of sulfur (S) are exposed to oxygen and water, being oxidized. In coal-mining areas, the most common of these minerals is iron pyrite (FeS_2); also the presences of acidophilic bacteria catalyzed these reactions. In FeS_2 case, AMD formation can be represented by the following equations:

$2FeS_2(s)+7O_2+2H_2O \rightarrow 2Fe^{+2}+4SO_4^{-2}+4H^+$ (Eq.1)

$2Fe^{+2}+1/2\ O_2+2H^+ \rightarrow 2Fe^{+3}+H_2O$ (Eq.2)

$2Fe^{+3}\ +6H_2O \leftrightarrow 2Fe(OH)_3\,(s)+6\ H^{+2}$ (Eq.3)

$14Fe^{3+}+FeS_2(s)+8H_2O \rightarrow 2SO_4^{-2}+15Fe^{2+}+16H^+$ (Eq.4)

The process is initiated with pyrite oxidation and release of ferrous iron (Fe^{+2}), sulfate (SO_4^{2-}), and hydrogen (H^+) (Eq.1). The sulfuroxidation reactions are catalyzed by bacterial metabolisms; where *Acidithiobacillus ferrooxidans* appears to be the main bacteria, especially because abiotic oxidation of iron is negligible at this pH values [3]. Next, ferrous iron undergoes oxidation forming ferric iron (Fe^{+3}) as equation 2 shows (Eq.2). Ferric ion is hydrolyzed by the reaction with water and formed ferric hydroxide $Fe(OH)_3$, an insoluble organic precipitant, and release additional acidity (Eq.3). The rate of $Fe(OH)_3$ formation is pH-dependent; it occurs rapidly when pH>4. Finally, further pyrite oxidation by ferric iron and another metals (Eq.4) [7,8].

These reactions can be produced in any time during the active mines, nevertheless, after when are closed and abandoned, the pumps turned off and are not anymore keep the water tables artificially low, then the water table can lead to contaminated groundwater being discharged, sometimes in a catastrophic event to human health an environmental [3,9]. A similar scenario occurs on low grade stocks, once the mining operation stops there no new material covering the stock, isolating from oxygen and humidity.

No matter it is an industrial bioleaching operation or AMD production, shows the same behavior, where Initial drainage has higher ionic concentrations and acidity and tend to get lower on time, dissolving any possible salt and metal from the ore. This means that when water refills the mine and dissolves any acidic salts that have built up on the pore spaces of the exposed walls and ceilings of underground chambers. This initial drainage water tends to be more potentially polluting (in terms of acidity and metal content) than AMD that is subsequently discharged [3,10].

Water with high metal concentration and strong acidity may be formed in mineral tailings and dump heaps, following the same reactions and biological phenomena than mine shafts and adits. Due to the more disaggregated state of ore when leaching ends, or higher concentration on tailings, or high "pyrite type" material on low grade stocks, AMD that flows from them may be more aggressive than discharges from the mine itself. The long term AMD production capacity is another issue to be concerned of, because AMD production may continue for many years after mines are closed and tailing dams are decommissioned. When talking about mine water discharges the terms "acid mine drainage" or "acid rock drainage" are used frequently, even when pH may be almost neutral (above 6), particularly at the point of discharge (where dissolved oxygen concentrations are frequently very low), this allows metals as iron and manganese to be as their reduced form (Fe^{2+} and Mn^{2+}), more stable than the complete oxidized form (Fe^{3+} and Mn^{4+}) at these pH. As water flows, oxygen might dissolved into it and decline its pH (not every AMD does). Net acidity has two components, the proton acidity (hydrogen ion concentration) and mineral acidity, dependent of concentration of soluble metals that produce protons when hydrolyzed. This particularity is used as an ore AMD production potential indicator, useful to create a closure plan for industrial operations [3,11,12]. In another hand, the alkalinity present for the bicarbonate deriving from the dissolution minerals or biological process can fall down the net acidity in AMD [3,4].

The showed reactions occur in a natural way in undisturbed rock, but at a very slow rate, and the water is able to buffer the acid generated. The mining produces an excess acid generation, beyond the water's natural buffering capabilities due to particle size reduction; hence increasing exposed surface area [4].

Characteristics AMD coming from different locations.

Tables 2 and 3 shows AMD characteristic from different localities, main pollutants correspond to high concentrations of iron, sulfate and other metals. In addition acidophilic bacteria that catalyze the generation of AMD are present. No information has been found, for Chile, but one could expect that AMD would have similar characteristics

	King's mine, Norway	Parys mine, United Kingdom	Cantareras, Spain	Richmon mine, USA
pH	2.7	2.5	2.7	0.5-1
Eh (mV)	-	285	425	-
Fe_{total}	171	650	1130	13-19 × 10^3
Fe^{2+}	-	650	915	13-19 × 10^3
Cu	16	40	160	120-650
Zn	25	60	24	700-2600
Sulfate	668	1550	1190	20-100<10^3
Moderate Fe-oxidizers	1 × 10^3	1 × 10^3	<10^2	-
Extreme Fe-oxidizers	6 × 10^4	3 × 10^3	1 × 10^5	-
S-oxidizers	<50	<10^2	<10^2	-
Heterotrophic acidophiles	2 × 10^4	2 × 10^3	<10^2	-

Table 2: Physic-chemical characteristics of AMD from various sites worldwide and associated microbial populations (Cupper mine).
All concentrations of metals and sulfate are shown in mg/L. Microbial counts are cells/ml and "-" means that numbers are not determined [13].

	Anna S, USA [14]	North West Province, South Africa [15]	China [16]
Mine Type	Coal	Copper-lead-zinc	Copper
pH	2.8-3.6	1.88	2.75
Al	Mar-36	-	
Fe	Jan-36	98.95	545
Mn	06-Sep	-	190
Zn	-	7.16	
Sulfate	-	4415.51	20800
Lead		2.35	
Copper		3.49	230

Table 3: Physic-chemical characteristics of AMD from various sites worldwide.

of the ore as previously indicated in the Table 1 [13,14,15].

Environmental problems causes by AMD

As we have indicated previously, AMD occurs by exposure of the metals sulphides to water and oxygen, causing major changes to water that receives the AMD. The oxidation of ores promotes the production of sulphuric acid and the release of a wide range of metals. The mixture causes serious environmental problems. AMD is toxic to aquatic organisms, destroys ecosystems, corrodes infrastructure, and taints water in regions where freshwater is already in short supply.

The impact of metals in water for humans as well as animals is the one hand, the persistence in the environment and the other hand, the accumulation in tissues, eventually causing chronic diseases. Usually, the disruption of metabolic functions by the metals is the cause of its toxicity, they accumulate in vital organs and they disrupt their important functions, and they inhibit the absorption, interfere with, or displace the vital nutritional minerals from their original place, thereby hindering their biological functions [16].

In plants experience oxidative stress upon exposure to heavy metals that leads to cellular damage and disturbance of cellular ionic homeostasis, in fact disrupting the physiology and morphology of plants. Plants need a proper balance of macro and micronutrients in the soil and thus the soil pH has an important influence on the availability of nutrients and on the growth of different kinds of plants [5].

It is widely know that aquatic organisms accumulate heavy metals from contaminated water and also by food. The big problems of the heavy metal are highly persistent and toxic even in trace amounts. The pH of water is important to aquatic life because it affects the normal physiological functions of aquatic organisms, including the exchange of ions with the water and respiration. Such important physiological processes operate normally in most aquatic biota under a relatively wide pH range (e.g., 6-9 pH). In fact, most of the freshwater lakes, streams, and ponds have a natural pH in the range of 6-8. When the ambient pH exceeds the range physiologically tolerated by aquatic organisms it can result in numerous sub-lethal effects and even mortality [5].

Chile regulation and legislation

In Chile, as in the rest of South America, the start of mining legislation begins with ordinances issued from Spain, promulgated in 1787, the "Ordinance of New Spain" becoming law in the Republic of Chile in 1833, remained in force until 1874. In 1932, it was performed some modifications, remaining in force for 50 years [17]. These documents lack environmental aspects to protect the surrounding ecosystem at a mine site. This changed in the 1990's, which was promulgated in 1992 Decree N°185, which seeks to regulate stationary sources of air pollution, in 1994 Law 19.300 of Environmental Framework, where the principle of promulgating "polluter pays" begins to be implemented and where an environmental impact assessment (EIA) is required for different types of businesses. In 2004, the Mining Safety Regulations required the submission of a closure plan. The Presidential Decree 248 issued in April 2007 ensures that the physical and chemical stability of the tailings deposits are such that they protect "people, property and the environment". In 2012, the new law (20,551) came into effect, which regulates mine closure and mining facilities. The main objective is to protect the life, health and safety of people and the environment, mitigate the negative effects of mining, hold accountable the mining industry job after cessation of operations, ensure the physical and chemical stability of ground where mining was developed, establish economic guarantees to ensure funding for the effective closure and post-closure monitoring chores of mining facilities [18].

AMD remediation

An abandoned mine than already started generating AMD can be considered a perpetual pollution producer. Since both oxygen and water are required to generate AMD, it follows that by excluding either (or both) of these, it should be possible to prevent or minimize AMD production [3,19]. Additionally, bacterial activity control prevents the contamination process from being catalyzed.

One way in which this may be achieved is by flooding and sealing abandoned deep mines. The dissolved oxygen (DO) present in the flooding waters (8-9 mg/l) will be consumed by mineral-oxidizing microorganisms present and replenishment of DO by mass transfer and diffusion will be impeded by sealing off the mine.

A technique widely used is to preventing contact between the mineral and dissolved oxygen, and consequent formation of AMD, is the flooding and sealing abandoned deep mines. The mineral-oxidizing microorganism consumed the dissolved oxygen (DO) present in the flooding waters, and the sealing of mine prevented the replenishment of DO by mass transfer and diffusion. However, this requires the knowledge of all shaft locations in order to be applied effectively and avoid influx of oxygen-containing water [3], and also know the huge water consumption inherent to this technique and the availability of this resource, making this technique unpractical for environment as northern Chile. The improved of this technique is by covering the tailings with a layer of sediment or organic material, to prevent oxygen ingress and some protection against re-suspension of the tailings due to the actions of weather [3,19,20].

Another suggested approach for minimizing AMD production is producing environmentally benign composites which acid consuming materials [21,22]. For example, in order to precipitate iron (III), as ferric phosphate is to add solid-phase phosphates (such as apatite) to pyritic mine waste; thereby reducing it's potential to oxidant of sulfide minerals [12]. But may only be temporary, then the application of soluble phosphate is with hydrogen peroxide, the peroxide oxidizes pyrite, producing ferric iron, which reacts with the phosphate to produce a surface protective coating of ferric phosphate.

The lithotrophic iron and sulfur-oxidizing bacteria the principle agents that perpetuate the generation of AMD are catalysts these reactions. Several laboratory and field tests using biocides have been carried out to inhibit their activities in mineral spoils and tailings, but the effectiveness has been found to be highly variable results and at best, only affords short-term control. Also the biocides are quite toxic and the effectiveness requires repeated applications. Is important further research for obtain a good tool against this kind of bacteria [3,11].

Even when these proposals work well in theory, the required quantities of resources such as water, effective sealing, biocides, etc., makes it unlikely to be applied everywhere. Most of Chilean operations are open pits located in the Atacama Dessert, driest desert on earth with an raining average of 2 mm/year. Therefore it is not practical to flood these sites in order to avoid contact between the minerals, water and oxygen. In fact there is water accumulating in the bottom of the open pit due its proximity to the water table.

This "sealing layer" that covers the spoil is usually constructed with clay, although in areas of the world that experience acute wet and dry seasons, drying and cracking of the cover can render it less effective than in temperate zones [23].

Given the practical difficulties mentioned above in inhibiting the formation of AMD at the source, there is the alternative of minimizing the polluting impact in receiving streams and rivers and the greater environment by controlling the spread of AMD and polluted water. In order to classify this processes the terms "active" and "passive" are commonly used. Conventional application consisting in the application of chemical products to neutralize and precipitate metals present in acid mine west, and latter to the use of natural and constructed wetland ecosystems. The difference between the process if is the application is continue active) or not (passive), in this case, obviously the active process is more expensive and require more maintenance than the passive process. In Figure 1, we show a brief summary of the remediation technology [24].

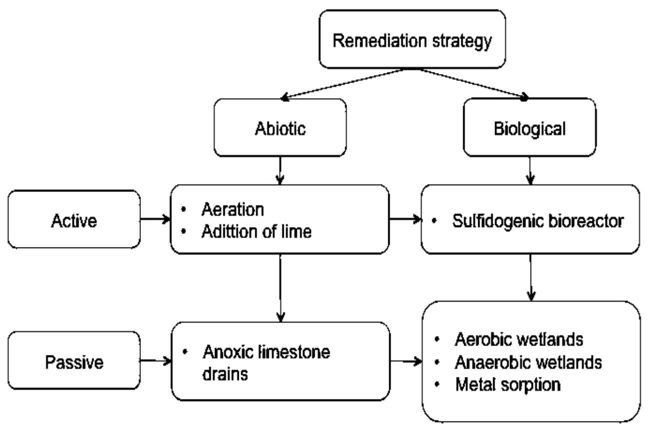

Figure 1: Acid Mine Water: Summary of remediation strategies.

Even when mining industries adopt just a few processes to treat all kinds of ores, the diversity of minerals it is possible to find in any given operation has lead to unique adaptations of these accepted processes, which results in unique waste. This type of wastes has forced researchers to adapt treatment processes as well, resulting in an endless list of possible treatments because each is focused on a particular contaminant or pollutant. The tables below show some of the considerations and comments about the main treatment alternatives (Tables 4 and 5) [25].

A summary of the techniques known in the remediation of AMD are displayed:

Abiotic process: The acid produced through mineral weathering can be buffered with alkalinity from treatment or natural sources; typically calcium carbonate, calcium hydroxide, or calcium oxide, are the neutralizing materials [26].

a. Active process: Maintain the stream with a pH over 6,5 and net alkaline conditions is the traditional goal for AMD treatment. This appears to be evident and still valid, even when the greater goal should be take back the stream characteristics to a pre-mining quality from a chemical and biological standpoint. Usually the design of AMD

Alternative	Considerations
Biotechnology	Usage of anaerobic sulfate reducing bacteria requires special conditions with constant nutrient feeding, pH, and temperature, is not economic option, which make it unlikely applicable at low costs without an important research work.
Separation using membranes (electrodialisis, reverse osmosis, ultrafiltration) and ionic interchanging resins.	These alternatives don't seem to be feasible because the effluent nature affects the membranes as much as the resins; it's expensive in large volumes. The main problems are high calcium and sulfate concentration that obstruct and destroy the base material of resins and membranes (polymeric or ceramic).
Evaporations and crystallization.	Even when these alternatives are actually possible from a technical point of view, it can be extremely costly given the large volume of effluent that needs to be treated.
Sulfate precipitation techniques (bario salts with/without regeneration and via etringgite formation.	Bario salt precipitation is feasible, but quite expensive. In former studies indicating FAD is efficient isolating $BsSO_4$, when adding sodium oleate. When forming etringgite, there are some patent and pilot tests, but none with an industrial application.

Table 4: Considerations about applying technologies [3,4,25].

Preventive methods	-Remove and/or isolate sulfur.
	-Remove oxygen from water sealing.
	-Remove oxygen from dry sealing.
	-Alkaline additives.
	-Bactericides.
Containing methods	-Avoid water flow.
	-Permeable reactive barriers (PRB) of reactive material located in the path of contaminants, considered as a passive treatment method.
	-Disposal in containment structure.
Remediation and treatment techniques	-Neutralization and precipitation of hydroxides and sulphur.
	-Separation by flocculation and flotation or lamellar settler.
	-Wetlands.
	-Remove sulfate and Mn^{+2} ions through co-precipitation.

Table 5: Prevention, control, treatment, and water usage from AMD [3,4,25].

treatment are based on the adding of enough alkali to buffer the stream, even when a neutral pH and a net alkaline conditions are necessary to achieve biological recovery, it is not always sufficient. This treatment strategy leads allows to recover the water chemistry and alkalinity, but produces lots of precipitated colloids and mineral as sulfates and iron hydroxides, affecting the habitat underwater trough the sediments cover of the streambed. Phenomena like this required to identify the possible depositional areas and settlement mechanisms to achieve a successful stream remediation [8].

b. Passive process: The Anoxic Limestone Drains (ALDs) can also be used to treat acidic waters, however, are not suitable of the treating all AMD, in the case of important concentrations of ferric iron, the half life of the process decrease until a few months. ALDs are limestone filled trenches through which acidic water is directed so the limestone can produce bicarbonate alkalinity via dissolution (Eq.5).

$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$ (Eq.5)

This kind of process is anoxic to prevent the contact of AMD with the oxygen and subsequent iron oxidation. The ALDs are capped with clay or compacted soil, to maintainer the anoxic conditions. Generally, ALD can be used as one component in the passive treatment, and also combined with another passive process by wetlands [3,7].

Biotic process: The biotic techniques are an option to remove contaminants using natural biological activity with the advantage of lower operating costs and clean technology.

a. Active process: Sulfogenic bioreactor: Sulfide minerals are also oxidized in a similar way, releasing metals and acidic sulfate in solution. Sulfate reducing bioreactors have become an economically viable alternative to conventional chemical processes for the treatment of wastewater that contains acid and metals. Sulfate reducing bacteria (SRB) have an ability to reduce sulfate to hydrogen sulfide, consumes protons while increased the alkalinity which leads it neutralization of the acid and produces stable precipitates of heavy metals, (Eq. 6 and 7) [11,27].

$SO_4^{2-} + 8e^- + 8H^+ \rightarrow H_2S + 2H_2O + 2OH^-$ (Eq.6)

$HS^- + M^{2+} \rightarrow MS_{(s)} + H^+$ (Eq.7)

Different kinds of anaerobic reactor have been employed in the biological removal of sulfate, using microorganism suspended and attached growth. The anaerobic baffled reactor, present an advantage because have a compartmentalized structure, which protect biomass of adverse environmental conditions, such as low pH and high metal concentrations.

b. Passive process: Passive treatment systems for acid drainage are intended to renovate and improve the quality of water that passes through them. In this point we including the use of the wetland by treated the AMD, for increased the pH and reduced iron and metal, present in the liquid as well, the potential use of biomass, for sequestering the metal present in the AMD [7,28].

Aerobic wetlands: This process is a kind of passive treatment system, simplest but is limited in the types of water they can treat effectively. These systems allow aeration to the mine water flowing among the vegetation. Dissolved Fe to oxidize, and to provide residence time where the water is slowed for Fe oxide products to precipitate. The AMD aerobic wetlands are used to treat mildly acidic or net-alkaline water containing elevated Fe concentrations, but have limited capacity to neutralize acidity; even the wastewater leaving the treatment may be pH lower than that entering [7].

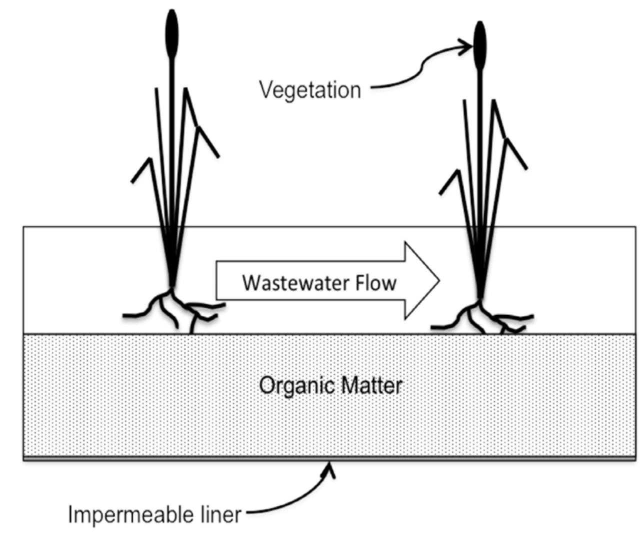

Figure 2: Aerobic wetland: Schematic representation.

A typical aerobic wetland system is a shallow trench planted with cattails (*Typha sp.*) (Figure 2). The depression that holds the wetland may or may not be lined with a synthetic or clay barrier. The iron-oxidizing bacteria oxidize iron at interfaces of aerobic and anaerobic zones. The plantation of macrophytes (e.g., *Phragmites australis, Typha latifolia, Juncus effusus*), the operation of the aerobic wetland is improved. In addition to achieving a regulation of the water flow, the iron oxidation is enhanced by the oxygen flow to the roots and by iron uptake of the macrophytes [7].

Anaerobic wetlands: To improve the treatment of the acid water, some changes have been made such as the addition of a bed of limestone beneath or mixed with an organic substrate, which encourages generation of alkalinity as bicarbonate. The biological sulfate reduction is a process that occurs under anoxic conditions (low O_2), whereby sulfate serves as the electron acceptor, this process also consumes protons while producing hydrogen sulfide (H_2S or HS^-), which leads to neutralization of the acidic pH by producing alkaline, and the precipitation of heavy metals, especially Fe and Al (Eq. 8). These systems commonly require large surface areas and long retention times because their effectiveness is limited by the slow mixing of the alkaline substrate water with acidic waters near the surface [7].

$SO_4^{-2} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$ (Eq.8)

The bicarbonate produced in the sulfidogenic oxidation increases the wastewater pH (Eq.8). Hence, metals and sulfate can be concomitantly removed and pH increased from acidic to neutral or alkaline in a single reactor. (Eq.9)

$M + H_2S \rightarrow MS(s) + H^+$ (Eq.9)

Biosorption: Conventional methods for removing metal ions from aqueous solution have been studied in detail, such as ion exchange, chemical precipitation, adsorption on activated carbon, electrochemical treatment, membrane technologies, etc. However, electrochemical treatment and chemical precipitation are ineffective, especially when metal ion concentration in aqueous solutions is as low as 1 to 100 mg L^{-1}, they also produce large amounts of sludge that can be difficult to treat, reaching the 40% of a urban wastewater reatment plan operational costs. Activated carbon adsorption process, ion exchange,

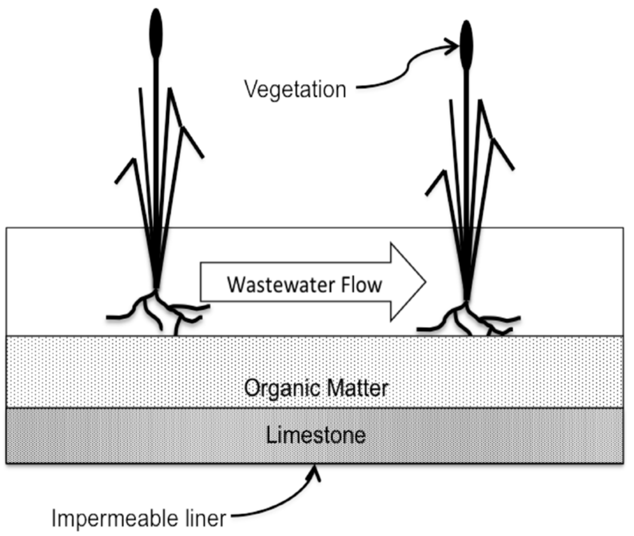

Figure 3: Anaerobic wetland: Schematic representation.

and membrane technologies are expensive, especially when treating a large amount of wastewater and water containing heavy metals at low concentrations [28].

An alternative process is biosorption. The bio-treatment for heavy metals generally includes bioaccumulation by dead or living biomass and the application of living biomass such as bacteria, algae, fungi, and seaweed as a biosorbent; this type of bio-treatment has emerged as a more cost effective process than other chemical processes and also as an eco-friendly process, which minimize byproducts. When dead biomass is immobilized in a polymeric matrix such as a bio-carrier, its presence confers high resistance to chemical environments and also provides additional advantages such as efficient regeneration and easy separation from solution [29] (Figure 3).

The biosorption process including the use of two phases, first one is a solid composed by biological material and a liquid phase (water). The liquid phase containing a species, witches are capable to be sorb, such as metal ion. The use of biomass for wastewater treatment has the advantage to be cheaper than traditional methods because of its availability in large quantities at low price [28].

The use of biosorption for a heavy metal remediation process in groundwater originating from AMD (pH lower than 4) has only been tested in laboratory tests, so further evaluation is required in the field to validate if the technique works effectively to remove heavy metals from AMD.

Phytoremediation: The phytoremediation is the use of green plants and their associated to microbiota, to remove the metals, contains ore renders environmental contaminants harmless [2,30]. Studies of phytoremediation have mainly focused on the removal of metals from contaminated soils, however there are new studies that have used hydroponics to assess the ability of plants to remove metals from aqueous environments (Klein). Indeed the *Thypa sp*. Used in the wetland methodology [25], several studies using *Phragmites australis* for phytoremediation, due is a typical wetland plant that can grow in aquatic system. The hydroponic experiments using synthetic AMD solution, concluding *Phragmites* is a species suitable for phytoremediation of polluted wetlands, because of its large biomass production, can remove considerable amounts of nitrogen and other macro elements, which accumulate in the leaves [31,32,33].

Copper Mining: Current Treatments

As mentioned previously, acid mine drainage (AMD) in Chile is one of the most important environmental issues facing the mining industry, as more than 95% of the copper mines in the country correspond to porphyry copper deposits, which are characterized by deposits and low grade bulk tonnage. These mines have generated and will generate millions of tons of waste rock dumps and debris, plus numerous large tailings dams. The issue of AMD in Chile is particularly relevant due to the new N°20.551 (modified by 20.819) Act of "mine closure", tending to establish rules about the closure process and responsibilities on the future, forcing the companies to take care of this issue.

Chile is home of El Teniente, the largest underground mine in the world, Chuquicamata, the biggest open pit operation worldwide, and Minera Escondida, the most productive copper mine in the world. The open pit walls and fractures (craters) in underground operations alone are expected to generate massive quantities of AMD. Some studies suggest that there is a production of sterile ore that is diverted directly to sterile ore dumps (<0.2% Cu) at a rate of 3,000,000 (ton/day) [34]. Flotation tails generate 1,000,000 (ton/day) and leaching dumps contribute 0.2-0.4% Cu all being important sources of AMD production.

Based on a study by the National Service of Geology and Mining (known as SERNAGEOMIN: *Servicio Nacional de Geologia y Minería*) within the framework of a collaborative project between Japan and Chile, known as FOCIGAM (Strengthening Institutional Capacity In Environmental Management In Mining) and published in 2007 [35], performed the first "National Registry of abandoned Mining Operations and/or Paralyzed", detecting 213 places where the level of pollution, rising to a total of 520 tasks abandoned by December 2013 [36].

Either as volunteer, forced by law or an early start for the closing, Chile has just a few examples and little experience in closing big mining operations, as listed below:

Mine Closure Plan "El Indio"

In 2002, "El Indio" mine ceased operations by depleting its reserves. After 20 years of operation and a total production of 5.5 million ounces of gold, 24 million ounces of silver, and 500,000 tons of copper, the mine, operated by Barrick, voluntary ceased production and closed the mine. Barrick invested more than US$80 million in the closure. Their plan considered [37].

- Ensure post-closure physical and chemical stability of the facility, in the long term.
- Minimize the impact on the quality and quantity of water from the Bad River, which flowed through the area.
- Ensuring the security of long term operation of the mine.

Mine Closure Plan "Lo Aguirre"

Pudahuel Mining Company Ltd., owner of "Lo Aguirre" mine, presented a voluntary closure plan in 2000. The plan considered the physical and chemical stability of the materials removed in order to protect the integrity and health of the surrounding population, natural resources, and environment. Pudahuel also considered other activities to mitigate the visual impact of the mine, which is near a major highway. This mine closure plan was funded by the remaining solutions containing copper, which is being recovered as a precipitate of 65% copper from scrap iron law [38].

Metal Recovery feasibility at "El Teniente", CODELCO, Chile

The origin of acidic water in the "*El Teniente*" division is due three factors inherent in an underground mining:

1. Abandoned sectors inside the mine (crater), a product of the progress of the operation.
2. The mineralized low grades overload this between the end of the exploitation of block and surface.
3. Rainfall, mainly the melting of snow in the craters formed over time.

Melting snow in the mining site provokes a natural leaching process of the exposed minerals on the surface. The acidic water contains between 1 and 2.5 g per pound with a pH of 2 or 3 and pools at the bottom of the abandoned pit.

The acidic water treatment (El Teniente) is performed in acidic water plant Sx-Ew (Solvent extraction-Electrowinning), which can operate in parallel (flow: 17oLjseg) or in series (flow: 25oLiseg); gg to produce cathodes, Cu g%. Investment Total of this project in 1984 was 17,350 KUSDI [39].

Sulfate Removal Plant "Punta Chungos", Los Pelambres.

The Punta Chungo plant in the mine Los Pelambres has the first plant in Chile to treat effluents using flotation to reuse water for irrigation. This plant removes sulfate ions, suspended solids, and molybdates, among others contaminants. The mine floor has an area of 760 m^2, the treated effluent concentrate filtration unit Los Pelambres flow in the order of 90 to 120 m^3/h. The unit is composed of two stages (two cells 6 × 4 × 1.5 m), one for the removal of sulfate ions and suspended solids in the second stage and the adsorption-ion molybdates co-precipitation of $Fe(OH)_3$ is removed. The ultimate goal is to reduce the molybdenum content of the effluent to 0.01 mg /L, the amount allowed by Chilean Standard Irrigation and Liquid Industrial Wasted (LIW) regulations. The separated sludge during flotation can be mixed with the copper concentrate, copper, and recovering stabilizing iron [4].

Conclusion

Chile has a huge environmental passive related to the AMD sources, due the lack of an standardization and law frame for the 520 mining abandoned facilities, but those are not the only sources as discussed above, active facilities has an important risk of becoming perpetual AMD sources too as sulfured ore copper grade decrease and low grade stock growth.

In the last decade Chile has made great strides in protecting the environment by establishing a series of laws that establish standards and guidelines for companies that impact the environment during their production processes. The Mine Closure Act lays the foundation for a sustainable mining development throughout the life cycle of a mining task.

Even when AMD production risks increase in the last years, due the precipitation increment as well as required copper grade to be processed (increasing production of low grade stocks), actual knowledge about the AMD production mechanism and industrial microbiology shows really interesting possibilities to treat and reuse AMD as well as avoiding its production. Nevertheless, and strong polity to support applied research appears as a requirement to integrate multidisciplinary research teams to considerer academic knowledge with mining experience in order to produce innovative and feasible solutions.

Even when the practical need of take care about AMD productions was always there, in almost every mining operation, the new law framework officially create the need for active mining operations, which is essential to avoid environmental passives increments and start being responsibly and unquestionably developing and sustainable mining.

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