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Use of Alternative Water Resources in Copper Leaching Processes in Chilean Mining Industry—A Review

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Abstract: Due to the significant growth of the world population, the accelerated growth of economic industries in various countries, and improved living conditions, freshwater consumption has increased dramatically and is currently under critical pressure. Its good use and rationing are essential. Even though mining is an industry that consumes much less water than other industries, such as agriculture, surrounding communities are constantly questioned. This occurs mainly because mining deposits are generally found in arid areas where freshwater is scarce, forcing government authorities to regulate water use in mining processes more severely. Faced with this scenario, the mining industry has innovated the use of seawater and wastewater from processes for its production processes. In addition, various projects are under development to construct desalination plants and water impulsion systems of the sea; therefore, it is expected that seawater and/or wastewater in mining will continue to grow in the coming years. Among the main challenges faced in the use of these water resources in mining is: (i) the close relationship that exists between the use of seawater and energy consumption, transferring the problem of water scarcity to a problem of energy cost overruns; (ii) generation of greater integration between the use of water and sustainable energy; and (iii) brine management is economically expensive and technically challenging and, therefore, most desalination plants discharge untreated brine directly into the sea, causing an environmental impact. On the other hand, regarding the use of these water resources in leaching processes, there are very positive results for the dissolution of copper from sulfide minerals, where the wastewater from desalination plants presents better results than seawater due to its higher concentration of chloride ions, allowing it to work at higher redox potential values in order to increase copper dissolution. This manuscript is a bibliographic review in which finally, it is concluded that it is feasible to incorporate wastewater from water desalination plants in heap leaching processes for copper sulfide ores, as long as the cost of transfer from water desalination plants to mining sites can be supported.

Keywords: seawater; wastewater; reject brine; leaching; copper mining

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1. Introduction

Water is the most precious and abundant resource on the earth's surface, covering 71% (oceans) of the planet's surface [1,2] and, in turn, is the habitat of 97% of living beings [3].

The oceans and other saline waters are the largest water resource on the planet, representing 97.4% of the available water [4,5]. The rest of the water (2.5%) corresponds mostly (1.7%) to polar and glacial caps, which is why it is not easy to use it. While traditional sources such as lakes, groundwater, and rivers, represent only 0.8% [4].

Freshwater is essential for all life forms and, in particular, for humans [6]. For example, the body of an embryo contains 97% water, the body of a newborn contains 80% water, and the body of an adult is 60–65% water [7]. If only the freshwater available on the planet is evaluated, the vast majority (68%) is enclosed in ice and glaciers, while the remaining 30% is underground [8]. Freshwater sources on the surface, such as rivers and lakes, only comprise about 93,100 cubic kilometers, equivalent to approximately 1/150 of 1% of the total water [7]. It should be noted that less than 1% of the total water available globally is freshwater that we can access easily, allowing us to satisfy our needs. Most of this water is replaced by precipitation through the water cycle [7,9,10].

Currently, freshwater resources worldwide are under critical pressure due to the great growth of the population, the accelerated growth of economic industries in several countries, and the improvement in people's living conditions, which implies more consumption of this resource [8]. Added to this is that water is distributed unevenly in almost all parts of the world [11]. Because of this, its use must be managed appropriately and used for long-term livelihood in the world [12]. An example of unequal distribution and low availability is the case of the Middle East and North Africa (MENA) region. This region is mainly arid and receives less than 1% of the earth's water. The annual share of water per capita in most countries belonging to this region is less than 200 m^3, which is unequal compared to the United Nations, where the poverty line is 1000 m^3/person/year [13].

According to calculations by the FAO (United Nations Food Organization), water resources exist "but if their management remains the same, there will be serious water scarcity crises in many parts of the world" [14]. Therefore, the challenges of managing this resource require adequate education, training, and public awareness on the management of water resources [12]. A clear example to follow is the case of Israel: even though most of its territory is desert, thanks to a long-term vision of the state and with an emphasis on R&D (research and development) it has managed to overcome this condition, even becoming surplus and to export this element to neighboring territories. It is the nation that recycles the most its water, around 85%, being a pioneer in the development of irrigation and desalination methods, but above all, it has fostered a culture among its citizens aimed at preserving water sources and avoiding their excessive spending [15–17].

Among the various industries that generate products for human use and consumption, agriculture is the one that uses the most water, accounting for 70% of the consumption of this resource, other industries use 20%, leaving 10% for human supply, at the same time that the growth of the world population is expected, which will also require water [18–21]. Among the various industries, one that continually generates controversy over its water consumption in its production processes is mining, although mining consumes much less water than agriculture. For example, the entire mining industry in Chile consumes 13 times less than the agricultural sector [22]. Despite this, most complaints about using this resource by local communities are directed at the mining industry. This occurs mainly because mining deposits are generally found in arid areas where freshwater is scarce, forcing government authorities to regulate water use in mining processes more severely [23–25]. Given this, the mining industry has innovated, in recent years, the use of seawater and wastewater from processes for its production processes. In this manuscript, a bibliographic review based on scientific publications in recent years is carried out on the acid leaching of copper sulfide minerals using seawater and wastewater from water desalination plants. This work aims to highlight the main problems and challenges presented by the mass implementation of these water resources in large-scale copper mining. For this manuscript, the case of Chile will be mentioned since it is the largest copper producer in the world and the country with the largest number of projects underway for the use of seawater and wastewater in mining.

2. Water Consumption in Chilean Mining

On a global scale, mining is a relatively small consumer of water. Still, usually, on a local scale, it is a large consumer of water. Mining is the fourth largest consumer of water in Chile, occupying 3% of the total [26]. The scarcity of fresh water in arid zones is an economical, environmental, and social problem [27]. In Chile, most of the national water consumption in mining (51%) occurs in the Antofagasta region, located in the Atacama Desert, which is the driest area in the country [4]. This situation generates conflicts between mining companies and nearby communities due to the shortage of available freshwater [28]. For this reason, the mining industry is driven to conserve the water it uses and minimize water discharge [5,29,30]. Toro et al. [5] mention that the General Water Directorate of Chile has expanded the areas of prohibition of water extraction, restricting water rights for mining companies, and that the country's authorities have established that large-scale mining projects would no longer be authorized to use water from aquifers. For this reason, the use of seawater or desalinated water has been considered in the new facilities, especially in the north of the country.

According to COCHILCO [31], by 2030, water consumption at the national level is expected to be 23.5 m^3/s, with an average annual growth rate of 2.7%. In general, the estimate of water consumption of continental origin is expected to reach 12.5 m^3/s by 2030, representing a decrease of 6% compared to 2020 (See Table 1). However, for seawater, the situation is different in that continental water consumption maintains an average annual growth rate close to −0.6%, whereas seawater grows with an average annual rate of 9.3%, reaching 11 m^3/s per year by 2030. By 2030, seawater consumption could increase by 120% compared to 2020, and seawater is expected to represent 47% of the water required by copper mining at the national level, as shown in Figure 1. This is a reflection, in part, of the change in the production matrix, which must be processed through flotation, a much more intensive process in the use of water. In addition, it is worth mentioning that there has been a drop in the grades of copper deposits in recent years, where currently, the grades are close to 0.5% of Cu [32,33]. Because of this, a greater quantity of water is necessary to obtain a ton of fine copper since it is necessary to process a greater quantity of ore.

Table 1. Projection of expected water consumption in copper mining (Data from: [31]).

Water (m^3/seg)	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030
Continental water	13.3	12.8	12.9	13.2	13.4	12.9	12.4	12.6	12.3	12.3	12.5
Seawater	5	5.6	7.5	8.2	9.2	9.9	10.6	10.9	10.7	10.9	11
Total	18.3	18.4	20.4	21.4	22.6	22.8	23	23.5	23	23.2	23.5

By 2030, the consumption of continental water by mineral concentration processes (MP) is expected to reach 73%, hydrometallurgical processes (LX + SX + EW) 5%, mine water and services (MW + S) 17%, and smelting and refining processes (F + R) 5%. This trend is maintained for seawater, where the highest consumption occurs in mineral processing (90% by 2030) (See Figure 1).

Mineral processing encompasses mineral comminution processes (crushing and grinding), flotation, classification, and thickening. The wastewater might be recirculated depending on the distance between the concentrator plant and the filtering and storage facilities. An important part of the water used in flotation becomes part of the tailings, sent to the thickening stage to recover a part of the water they contain.

In the mine area, either open-pit or underground, and the transport of the material to primary crushing, the water is used mainly to suppress dust on roads and in the extraction and pumping from work underground. The services area comprises those activities with insignificant volumes of water consumption compared to the total consumed in a mining operation. The main use of water is for drinking, cooking, washing, irrigation,

and bathing in the camps, molybdenum plants in operations that have them, and other minor consumptions.

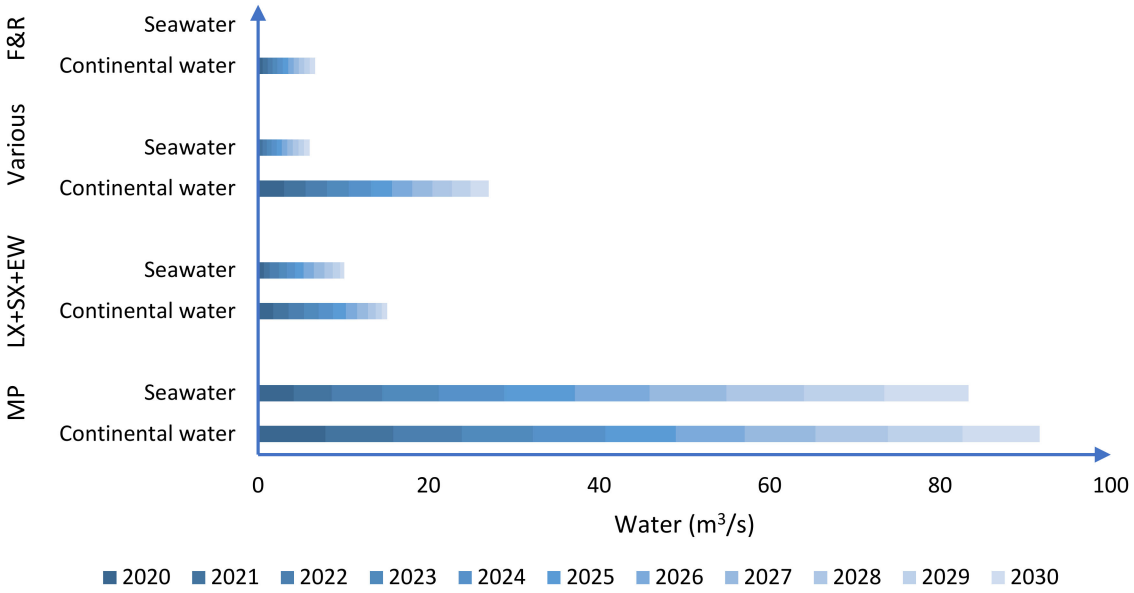


Figure 1. Distribution of water consumption according to mining process. (MP: mineral processing; LX: leaching; SX: solvent extraction; EW: electrowinning; F&R: smelting and refining processes (Data from: [31])).

In hydrometallurgical processes that consider heap leaching, solvent extraction, and electrowinning processes, the primary water consumption results from the evaporation of the leaching solution (sulfuric acid + water) in the leaching piles.

3. Seawater

Currently, the use of seawater in production processes is an alternative to the limited availability of water resources. Many mining companies are beginning to use seawater in their industrial processes. Some use it directly in their processes, and others desalinate it to introduce them to their plants later. Incorporating seawater into copper production processes causes changes in the equilibrium of the solutions and their physical-chemical properties. Among the operational problems and consequences associated with the use of seawater in the industry are:

- The presence of salts in seawater influences the properties of the system and affects metallurgical efficiency [34].
- It can produce fouling in the equipment, plugging of pipes, and/or precipitation of salts [35].
- Development of algae and microalgae in the equipment and pipes of the facilities, which introduces unwanted material to the process [36].
- Water pretreatment costs [37–40].
- Corrosion of the equipment due to the high concentration of chlorides. This implies adopting mitigation strategies, which translates into high investment capital and a higher maintenance cost due to corrosion [41].
- High cost in transportation since most companies are at a great height with respect to sea level, which translates into a higher cost in infrastructure and energy [42].

Among the alternatives or solutions to the recently raised problems are [43]:

- Desalination through evaporation or filtration equipment using high-pressure membranes to remove salts.

- Add sodium hypochlorite, produce chlorine gas by electrolysis, use ultraviolet light, among others, to remove organic material.
- Use special anti-corrosion materials such as carbon steel, coated steel, HDPE (high-density polyethylene), FRP (fiberglass reinforced plastic).

For the use of seawater in mining processes, the following steps are followed (see Figure 2):

- It must first be collected from the shore;
- Then, it is pretreated (desalinated) (this option depends on the process of the mining site);
- Subsequently, it is transported by pumping systems;
- Moreover, finally, it is used in the process of the mining company.

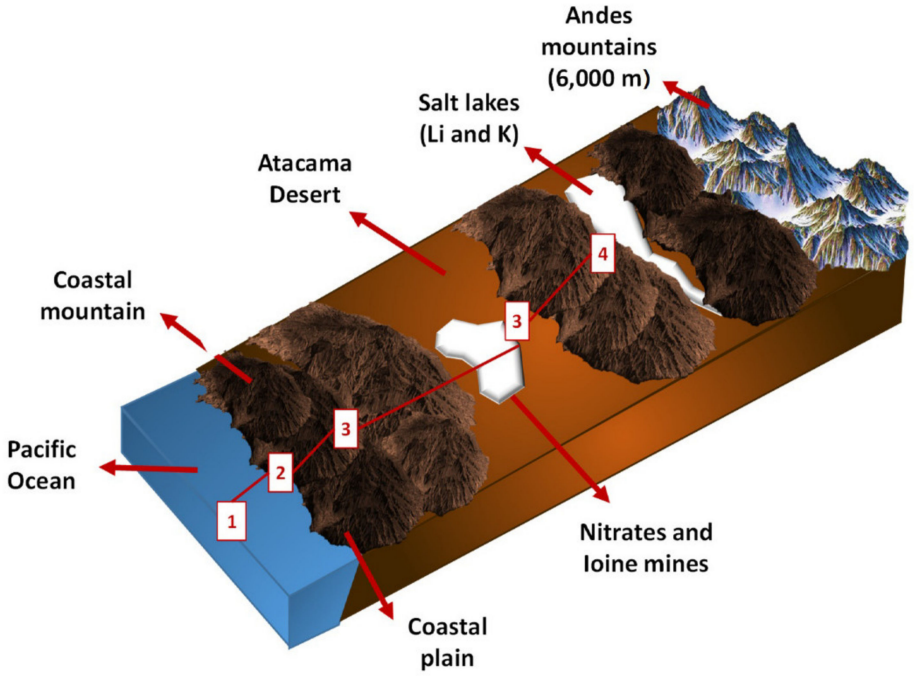


Figure 2. Geographic scheme of the Antofagasta region in Chile, mining activities and seawater collection system (Modified from: [4]).

For leaching processes, various studies have been developed using seawater for the dissolution of primary copper sulfides [44–49] and secondary copper sulfides [5,26,34,50,51]. In general, there is a consensus in all the studies regarding the positive effect generated by incorporating seawater in leaching processes. This is mainly due to its chloride ion concentration (~20 g/L) [52] (See Table 2). The high dissolution rate in the chlorinated system compared to the sulfated system is attributed to the ability of the chloride ion to stabilize the cuprous ion through the formation of $CuCl_3^{2-}$. In the chloride system, copper can be extracted directly from the chalcocite without the oxidation of Cu^+ to Cu^{2+}. In the sulfated system, Cu^+ must be oxidized to Cu^{2+} on the surface before the copper is released to the solution [53]. The addition of chloride ions not only allows the passivated sulfur layer to be broken since an increase in the concentration of chloride ions implies an increase in the redox potential [54], and a higher redox potential generates a thinner layer that makes it easier for chloride ions to generate porosity.

Table 2. Reference composition of seawater (data from [5]).

Solute	g/kg of Solution	Solute	g/kg of Solution
Na^+	10.78145	Br^-	0.06728
Mg^{2+}	1.28372	CO_3^{2-}	0.01434
Ca^{2+}	0.41208	$B(OH)_4^-$	0.00795
K^+	0.3991	F^-	0.0013
Sr^{2+}	0.00795	OH^-	0.00014
Cl^-	19.35271	$B(OH)_3$	0.01944
SO_4^{2-}	2.71235	CO_2	0.00042
HCO_3^-	0.10481	Total	35.16504

Hernández et al. [46] investigated the effect of the addition of sodium and potassium nitrate for the leaching of chalcopyrite in an acid medium (H_2SO_4), comparing the use of distilled water and seawater. The researchers evaluated the concentration of sodium nitrate in the system where they observed positive results, achieving an increase in copper extraction from 27.9 to 80.2% in media based on seawater and from 14.8 to 63.9% in media based on distilled water, this is due to the oxidizing potential of nitrate ions (see Figure 3).

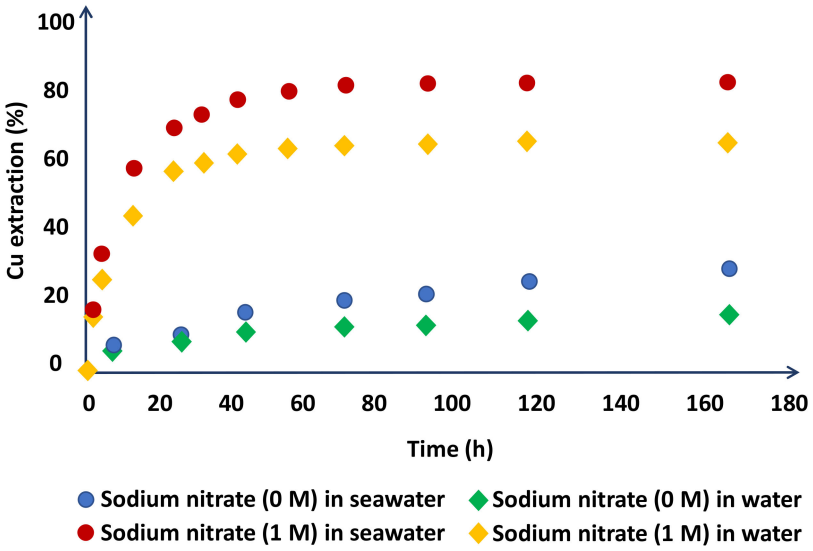


Figure 3. Chalcopyrite dissolution in the leach liquors using H_2SO_4 (1 M) + $NaNO_3$ (0 or 1 M) in seawater- and water-based media (at 45 °C) (Modified from: [46]).

Regarding the acid concentration, Hernández et al. [46] showed that it is possible to achieve similar copper extractions when working at 0.5 M H_2SO_4 in seawater compared to working with 1 M of H_2SO_4 in distilled water (see Figure 4). This agrees with the results reported by Senanayake [55], Cerda et al. [45], and Castellón et al. [44] who indicate that the presence of salts such as NaCl, $CaCl_2$, or $MgCl_2$ increases the activity of H^+ protons, allowing it to work at lower acid concentrations. In addition, Castellón et al. [44] indicate that ion oxidation increases with higher acidity levels in the leaching solution due to the formation of NOx gas after a long time. The researchers report that the formation of this gas allowed the system's potential to be maintained at values over 700 mV vs. Ag/AgCl, facilitating the leaching of chalcopyrite (see Figure 5).

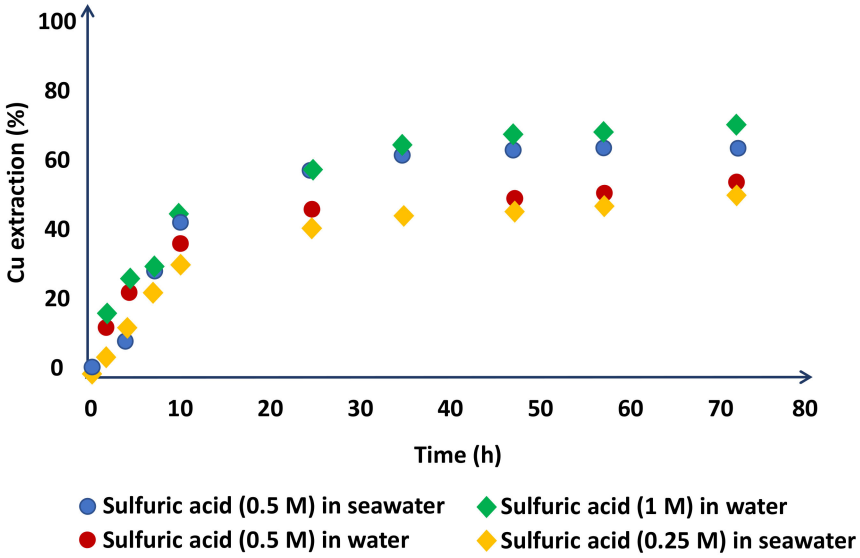


Figure 4. Chalcopyrite dissolution in the leach liquors with experimental conditions of $NaNO_3$ (1 M), three days of leaching, 45 °C (Modified from [46]).

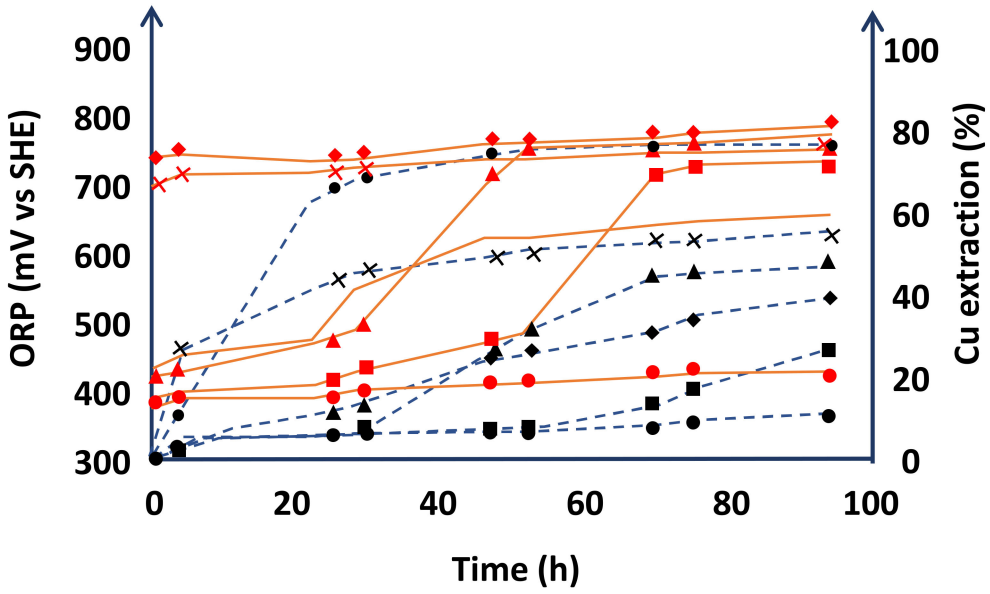


Figure 5. Dissolution of chalcopyrite concentrate and averaged ORP (mV vs. Ag/AgCl) values over time (hours) for Series I at different concentrations of H_2SO_4 and NaNO3. (o) Test 1 (H_2SO_4 = 0.1 M and $NaNO_3$ = 0.1 M); (■●◊Δ○●) Test 2 (H_2SO_4 = 0.1 M and $NaNO_3$ = 0.5 M); (N) Test 3 (H_2SO_4 = 0.5 M and $NaNO_3$ = 0.1 M); (●) Test 4 (H_2SO_4 = 0.5 M and $NaNO_3$ = 0.5 M); (X) Test 5 (H_2SO_4 = 1.0 M and $NaNO_3$ = 0.1 M); (_) Test 6 (H_2SO_4 = 0.5 M and $NaNO_3$ = 0 M). (Test conditions: 94 h, P80 = 60.66 µm, 450 rpm and room temperature). The copper recoveries are shown with black dotted line in axis secondary and averaged ORP values are shown with red dotted line (Modified from: [44]).

On the other hand, in the experiments carried out by Hernández et al. [56] for the leaching of a chalcopyrite concentrate in an acid medium, using seawater and caliche salts, the researchers compared the effect of adding NaCl to the same proportion of chloride than seawater (See Figure 6a). Their results showed that the copper extractions for both cases are almost identical, which confirms that the chloride ion influences the seawater leaching system, and not the other ions present, such as the fluoride and bromide ions. Furthermore, in Figure 6b, it can be seen that both systems have similar behavior in their potential redox values. This is consistent with the study carried out by Toro et al. [5] to leach chalcocite in

an acid medium using seawater. The researchers obtained similar results when working with seawater and chloride at 20 g/L (see Figure 7).

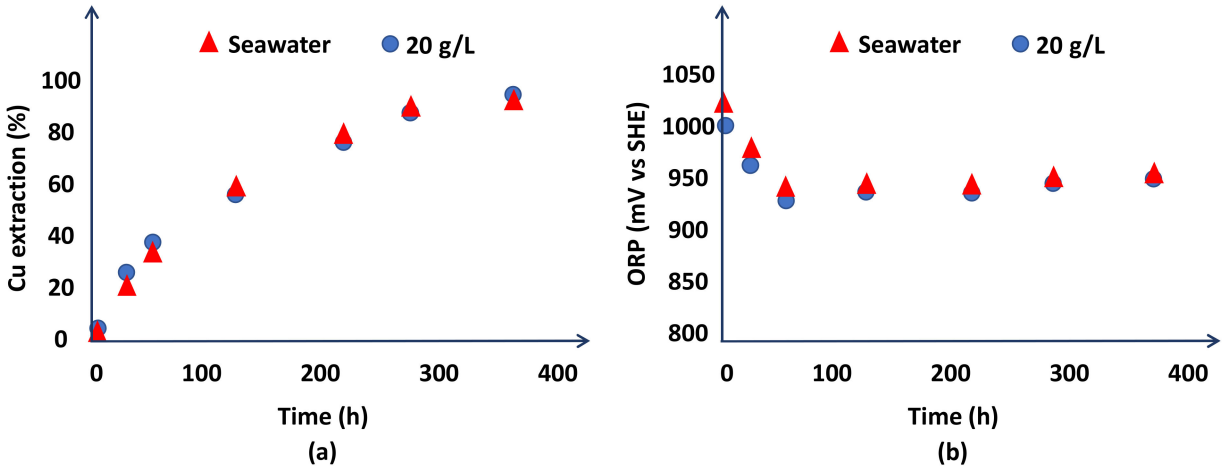


Figure 6. (**a**) Comparison of copper extraction (%) curve when seawater and water with 20 g/L Cl^- were used as water sources in the leach solution. (**b**) Redox potential (mV) versus time (h) when seawater and water with 20 g/L Cl^- were used as a source of water in the leach solution. Experimental conditions: $[NaNO_3] = [H_2SO_4] = 0.7$ M, 45 °C and sample A. (Modified from: [57]).

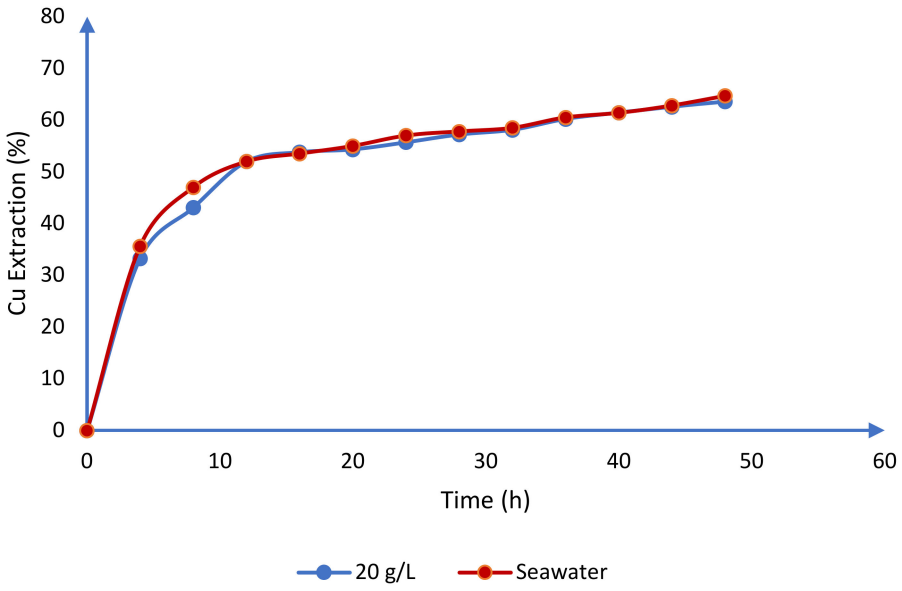


Figure 7. Comparison between the use of seawater and synthetic chloride (20 g/L) for the dissolution of chalcocite in an acid medium (T = 25 °C, H_2SO_4 = 0.5 mol/L) (Modified from: [26]).

4. Discard Water

The scarcity of water and the consumption of this resource generated by large-scale mining in hyper-arid areas of Chile caused restrictions by government entities for the use of aquifer waters. The generation of new facilities that consider the use of sea or desalinated water has been promoted [58]. There are currently 14 water desalination plants that are associated with mining operations (see Table 3) and other future projects (see Table 4).

Table 3. Land registry of desalination plants and seawater impulsion systems in copper mining in operation (Data from: [59]).

Mine	Desalination Capacity (L/s)	Seawater Use Capacity (L/s)	Length of Water Transport Pipes (km)
Michilla	75	23	-
Planta J.A. Moreno (Taltal)	-	15	-
Las Cenizas (Taltal)	9	12	7
Mantos de la Luna	20	5	8
Pampa Camarones	-	25	12
Centinela	50	1500	145
Cap Minería	600	-	120
Escondida (Planta Coloso)	525	-	180
Antucoya	20	280	145
Candelaria	300	-	110
Mantoverde	120	-	42
Sierra Gorda	-	1315	142
Escondida EWS	2500	-	180
Candelaria	700	-	110

Table 4. Future projects of desalination plants and seawater impulsion systems in copper mining (Data from: [60]).

Mine	Desalination Capacity (L/s)	Seawater Use capacity (L/s)	Length of Water Transport Pipes (km)	Start-Up Year
Los Pelambres	400	-	150	2021
Spence Growth Option	800 (1600 potential)	-	154	2021
MantoVerde	Add 260 to current capacity	-	42	2022
ENAPAC (Múltiples mineras de la zona norte de Chile)	2630	-	-	2022
Quebrada Blanca	850 (1200 potential)	-	160	2023
CODELCO (Chuquicamata, Radomiro Tomic y Ministro Hales)	840 (1956 potential)	-	160	2023
Santo Domingo	30	400	112	2024
COLLAHUASI	525 (1050 potential)	-	195	2024
Diego de Almagro	-	315	61	2025
Centinela	-	1650	145	2025
El Abra	500	-	-	2027
Nueva Unión	700	-	-	2028

The water desalination processes generate a waste known as brine returned to the sea in large quantities with a higher chemical element concentration (See Table 5). In addition, brine has a higher density than seawater. Because of this, it cannot mix with the sea, decanting at the bottom of the ocean [61–64]. Additionally, it should be mentioned that the water desalination process requires electricity as energy, which in turn requires fossil fuels. In the case of Chile, coal is used. For 1000 m^3/day of desalinated water, it is necessary to burn 10,000 tons of oil per year, resulting in environmental pollution through greenhouse gas emissions [65]. To solve this problem (contamination), the ENAPAC project is under development in Chile, consisting of a self-sustaining seawater desalination project that will be supplied with photovoltaic energy. ENAPAC considers the largest desalination plant in Chile and Latin America due to its maximum capacity of 2630 L/s. It will also be the first plant to supply various mining companies at the same time, the only large-scale

plant with solar energy (100 MW), and one of the most advanced projects in the world with a combination of desalination by reverse osmosis and photovoltaic energy [59,60].

Table 5. Composition of wastewater from desalination plants used in previous studies.

Previous Research	**[5]**	**[57]**
Compound	Concentration (g/L)	Concentration (g/L)
Fluoride (F^-)	0.002	0.002
Calcium (Ca^{2+})	0.8	0.4
Magnesium (Mg^{2+})	2.65	2.29
Sodium (Na+)	20.85	19.77
Potassium (K+)	0.82	0.75
Bicarbonate (HCO_3^-)	1.1	0.236
Chloride (Cl^-)	39.16	36.07
Calcium carbonate ($CaCO_3$)	13	10

Various works have been developed to treat sulfide minerals in acidic media in recent years, reusing wastewater from water desalination plants (see Table 6). This is mainly due to its high concentration of chloride ions, which can reach 60 g/L, depending on how many cyclical desalination processes it has received. Its high saline concentration could be used favorably in the dissolution of sulfide minerals, thus giving rise to an eventual water resource.

Table 6. Comparison between previous investigations for the dissolution of copper sulfide minerals in an acid medium using wastewater.

Research	**Mineral**	**Leaching Agent**	**Parameters**	**Cu Extraction (%)**	**Reference**
Influence of seawater and discard brine on the dissolution of copper ore andcopper concentrate	Copper Oxides (Atacamite and Chrysocolla), Chalcopyrite Concentrate, Chalcopyrite Mineral	H_2SO_4, NaCl, Discard salts	Chloride concentration, cure time, potential redox variation in the leaching solution	92	[49]
Leaching of Pure Chalcocite in a Chloride Media Using Sea Water and Wastewater	Chalcocite	H_2SO_4, NaCl	Chloride concentration, acid concentration	67.75	[26]
Leaching of Pure Chalcocite in a Chloride Media Using Wastewater at High Temperature	Chalcocite	H_2SO_4, NaCl	Acid concentration, chloride concentration, temperature	97	[50]
Caliche and Seawater, Sources of Nitrate and Chloride Ions to Chalcopyrite Leaching in Acid Media	Chalcopyrite	H_2SO_4, $NaNO_3$, NaCl	Temperature, solid/liquid ratio, chloride concentration, particle size, nitrate concentration, acid concentration, cure time	92.3	[57]
Dissolution of pure chalcopyrite with manganese nodules and wastewater	Chalcopyrite	H_2SO_4, NaCl, MnO_2	stirring speed, acid concentration, MnO_2 concentration, potential variation in the leaching solution	77	[5]
Leaching Chalcopyrite with High MnO_2 and Chloride Concentrations	Chalcopyrite	H_2SO_4, MnO_2	Particle size, temperature	71	[25]

Table 6. *Cont.*

Research	Mineral	Leaching Agent	Parameters	Cu Extraction (%)	Reference
Use of Seawater/Brine and Caliche's Salts as Cleanand Environmentally Friendly Sources of Chloride and Nitrate Ions for Chalcopyrite Concentrate Leaching	Chalcopyrite concentrate	H_2SO_4, caliche salts	Acid concentration, nitrate concentration, chloride concentration, temperature, cure time	90.6	[56]
Leaching of Pure Chalcocite with Reject Brine and MnO_2 from Manganese Nodules	Chalcocite	H_2SO_4, NaCl, MnO_2	chloride concentration, acid concentration, potential redox variation in the leaching solution, MnO_2 concentration	71	[58]

Velásquez-Yévenes and Quezada-Reyes [49] indicated that chloride ions do not influence the leaching of oxidized minerals. Their experiments obtained copper extractions of 90% for all cases, independent of the chloride concentration in the system. Therefore, the use of seawater or wastewater does not improve the leaching of oxidized minerals. On the other hand, in their experiments for a chalcopyrite mineral, through a previous process of agglomeration and curing, and subsequent leaching in columns, the authors indicated that when working with 100 days of curing, better extractions are obtained with the wastewater (43%) compared to seawater (37%) in 80 days of irrigation. This agrees with the study carried out by Hernández et al. [57]. The authors compared the use of distilled water, seawater, and wastewater to leach chalcopyrite, using nitrate ions as an oxidizing agent, obtaining the highest copper extractions with wastewater (see Figure 8).

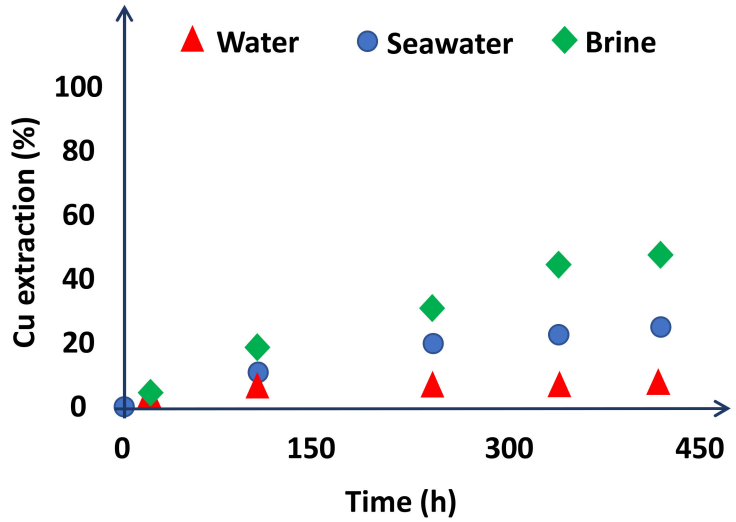


Figure 8. Copper extraction (%) versus time (h) when different dissolvents were used: distilled water (water), seawater, and brine. Experimental conditions: [$NaNO_3$] = 0.7 M, [H_2SO_4] = 0.7 M, −150 + 75 µm, S/L ratio 2 g/L, 45 °C, 350 rpm, sample A. (Modified from: [57]).

It is important to mention that, in most studies where chalcopyrite mineral or concentrate is leached, either with seawater or discards, they have worked at moderate temperatures (40–90 °C) due to the passivation that is generated from the formation of a passivating layer that prevents contact with the reactant [66–69]. In a study carried out by Toro et al. [5], wastewater and high concentrations of MnO_2 in an acid medium were used to dissolve $CuFeS_2$. The authors indicate that it is possible to dissolve chalcopyrite at room temperature and avoid passivation when working at high chloride concentrations (~40 g/L) and

$MnO_2/CuFeS_2$ ratios of 4/1 or higher (see Figure 9). The researchers indicate that under these operational parameters, it is possible to keep the potential stable in a range between 580 and 650 mV, achieving Cu extractions of 77% when working at $MnO_2/CuFeS_2$ ratios of 5/1 and a concentration of 1 mol/L of H_2SO_4 at 25 °C (see Figure 10). In addition, an analysis was carried out on the residues obtained, where the formation of polluting elements such as stable elemental sulfur did not occur, and other elements present such as MgO and $CaSO_4$ did not affect the extraction of Cu (see Figure 11). Later, in the study carried out by Torres et al. [25] under the same operational conditions as in the previous study carried out by Toro et al. [5] but evaluating the influence of temperature on the system, the researchers indicate that there is no synergy between the high concentration of MnO_2 in the system and moderate/high temperatures, with the presence of MnO_2 in the system being irrelevant when working at temperatures of 80 °C or higher.

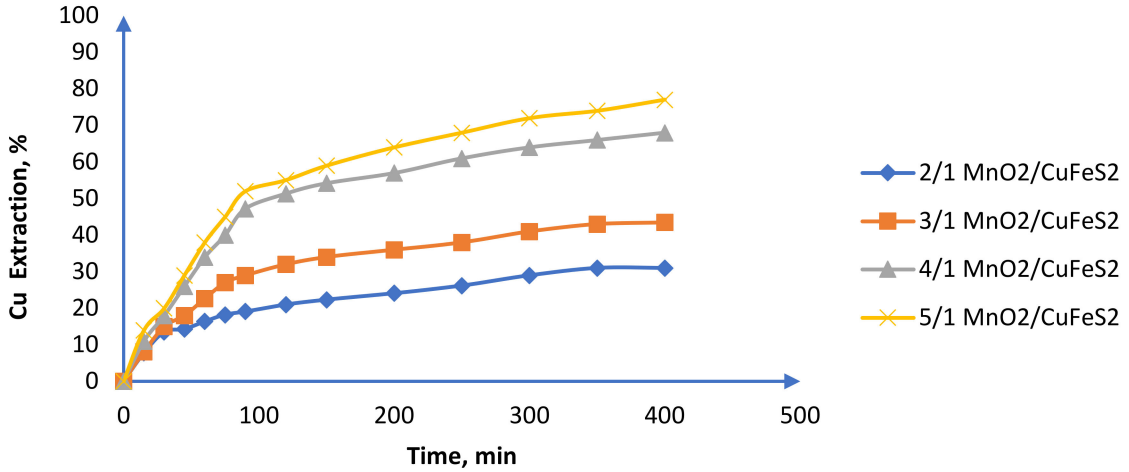


Figure 9. Effect of the $MnO_2/CuFeS_2$ ratio on Cu extraction (25 °C, $CuFeS_2$ size: −47 + 38 m, MnO_2 size: −75 + 53 m, 1 mol/L H_2SO_4 and 39.16 g/L of chloride) [5].

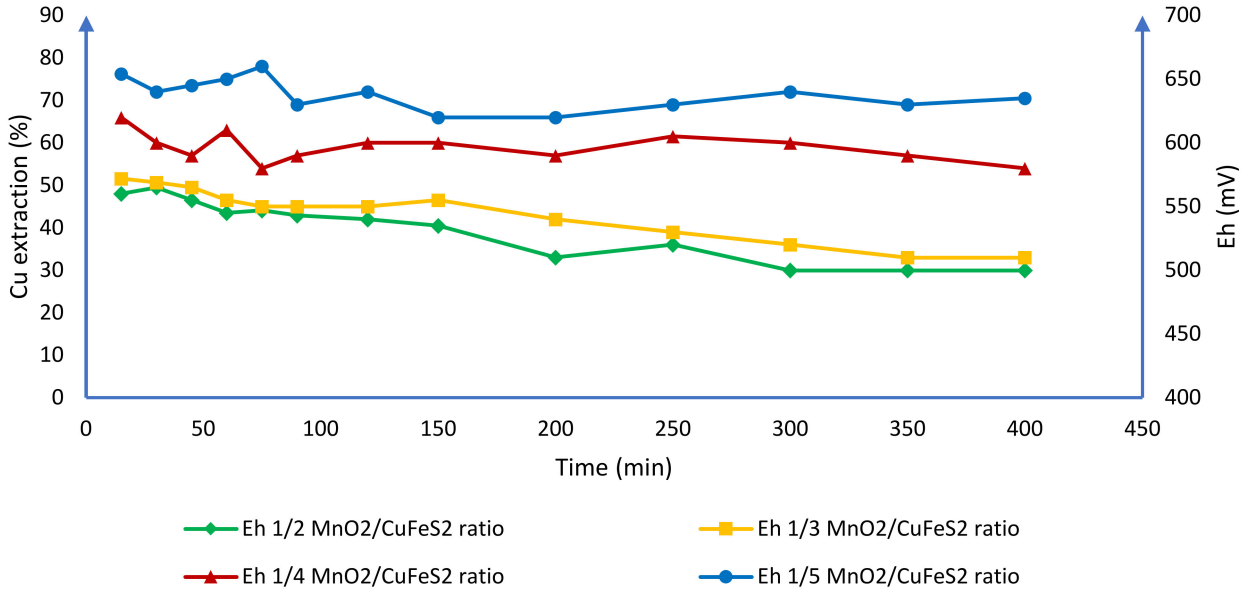


Figure 10. Effect of the potential in the solution of Cu at different ratios of $MnO_2/CuFeS_2$ [5].

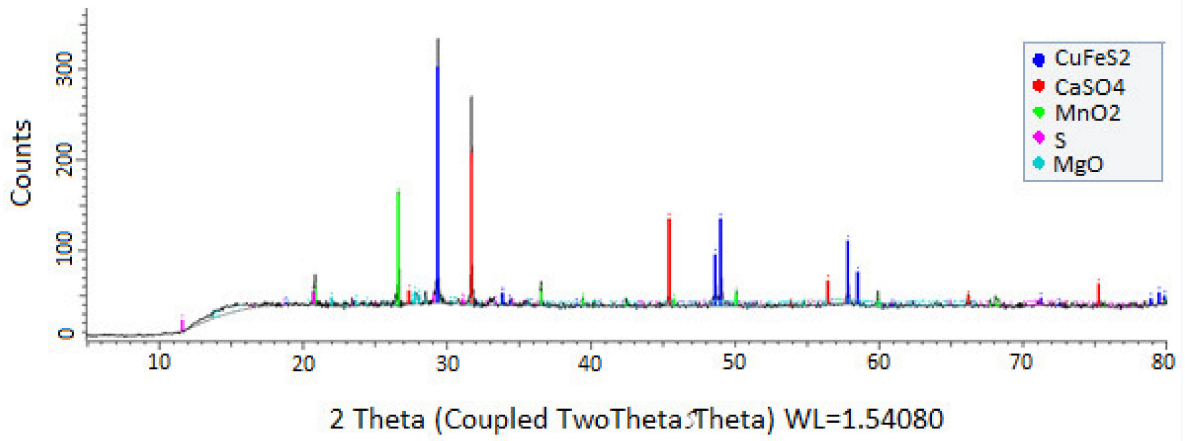


Figure 11. X-ray powder diffraction patterns for the residue mineral after being leached with wastewater at 25 °C in a time of 90 min. $CuFeS_2$ size: −47 + 38 µm, MnO_2 size: −75 + 53 µm, $MnO_2/CuFeS_2$ to 5/1 and 39.16 g/L chloride) [5].

Regarding secondary sulfide leaching, Toro et al. [26] carried out an acid leaching of chalcocite by comparing the use of seawater and wastewater. Initially, the researchers conducted a statistical study (ANOVA analysis) to evaluate the effect of acid concentration, chloride ion concentration, and leaching time. Their results indicate that the acid concentration has little influence on the Cu_2S dissolution, being more important to work at high chloride concentrations in the system. Finally, the researchers indicate that when chalcocite is leached in a chlorinated system (seawater and/or waste), it has a rapid dissolution (exponential) until reaching a 50% extraction of Cu, which is due to the subsequent formation of covellite, which has lower dissolution kinetics. Therefore, better results are obtained when working with wastewater because they allow for a greater redox potential in the system due to its higher concentration of chloride ions, favoring the dissolution of CuS in the second leaching stage. Subsequently, the study carried out by Torres et al. [58] worked under the same operational conditions as Toro et al. [26] but testing the addition of MnO_2 as an oxidizing agent to the system. In their work, the researchers concluded that adding MnO_2 at low concentrations to the system significantly improves the extraction of Cu from Cu_2S in short periods, which is important in continuous leaching operations (See Table 7).

Table 7. Comparison of chalcocite dissolution with reject brine and the effect of MnO_2.

Experimental Conditions and Results	[26]	[58]
Temperature (°C)	25	25
Particle size of Cu_2S (um)	−147 + 104	−147 + 104
H_2SO_4 concentration (mol/L)	0.5	0.5
MnO_2/Cu_2S ratio (w/w)	-	0.25:1
Dissolution in seawater after 4 h (%)	32.8	35.6
Dissolution in reject brine after 4 h (%)	36	40
Dissolution in seawater after 48 h (%)	63.4	64.7
Dissolution in reject brine after 48 h (%)	64.6	66.2

5. Conclusions

From the point of view of the behavior of the projection of seawater in mining processes, there are various projects of desalination plants and systems of impulsion of seawater to feed the mining works by the year 2030. To this are added the restrictions on the use of fresh water in large copper mining by government entities. Therefore, it can be concluded that the use of seawater and/or wastewater in mining will continue to boom in the coming years.

On the other hand, the use of seawater and desalination plants has been of great help in the face of the scenario of water shortage and the availability of water for mining

operations, also contributing to dewatering inland water sources, the challenges that this type of technology entail are as follows:

The close relationship between seawater and energy consumption, transferring the problem of water scarcity to a problem of energy cost overruns. For example, in Chile, seawater must be driven to sites located more than 2000 m above sea level and with pipes that measure between 150 and 200 km.

Based on the previous point, greater integration between water and sustainable energy should be generated. The reuse of water, combined with integrated management by basins, could solve the shortage observed in highly vulnerable basins located in environment aggregates.

Even though desalination can provide a supposedly unlimited and safe supply, independent of the weather, there are specific challenges to harnessing the potential of desalinated water, such as environmental impacts. Handling brine is economically expensive and technically difficult, and therefore most desalination plants discharge untreated brine directly into the environment.

Regarding its use in leaching processes, seawater is a resource that is currently incorporated in mining and presents good results due to the chloride ions present in it. On the other hand, the wastewater from desalination plants has shown, in the various studies published in recent years, better results for the dissolution of copper from sulfide minerals, which is because it has a higher concentration of chloride ions than seawater (approximately double), which allows the system to work at higher redox potential values. It is also important to mention that the higher chloride content of the wastewater compared to seawater does not cause problems in the subsequent process (solvent extraction). Additionally, it is important to mention that when working with the two mentioned water resources in sulfur mineral leaching processes, the residues that are generated do not present the formation of polluting elements. Therefore, it can be concluded that it is feasible to incorporate wastewater from water desalination plants in heap leaching processes for copper sulfide minerals, as long as the cost of transferring from water desalination plants to the mining sites can be supported.

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