Chapter 6

Innovative Solutions for Seawater Use in Mining Operations

Edelmira D. Gálvez and Luis A. Cisternas

Additional information is available at the end of the chapter

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Abstract

This chapter reviews the use of seawater in the mining industry in Chile, especially from the perspective of the current situation and the innovative proposals for its sustainable use. This chapter describes the current use of seawater, with and without desalting, in the mining sector in Chile, as well as its future projection. Descriptions are given for the current desalination systems, mining operations currently using seawater and new projects, current water distribution systems, seawater applications in hydrometallurgy and minerals concentration, their environmental impacts, and difficulties in adapting processes in case of use of seawater without desalination. This is complemented by a description of mining in Chile, its importance for Chile and its relationship to the global mining. Finally, problems and opportunities are identified. A second aspect considered in this chapter is the innovative solutions that are being investigated to solve some of the problems indicated above, including integrated seawater distribution systems, seawater bio-desalination, partial desalination using carbon dioxide, adaptation of process to the use of seawater without desalination, and uses of discard brines from reverse osmosis plants.

Keywords: mining, desalination, seawater, water distribution networks, Chile

1. Introduction

The major resource of water on the planet is the water in the oceans that represent 97% of available water. The other 3% includes a 2% of available water in ice caps and glaciers and therefore is difficult to use as a water resource. Traditional freshwater resources (groundwater, lakes, wetlands, rivers, among others) represent only 1% of all water on the planet. Overexploitation of these traditional resources in arid and semiarid areas, such as northern Chile, southern Peru, and parts of North and South Africa, Asia, and Australia, has created a situation of scarcity of the resource that forces them to seek new water sources and improve the efficiency of its use.

Water has become an important research topic since a significant part of the world is not managing to have this resource of adequate quality and because the different sources of water on the planet are affected by human activities. Thus, the publications registered in web of science that include in the title the word "water" have increased from 10,601 to 24,925 from the year 2000 to 2016. As the main source of water is the water in the oceans, research related to seawater has proportionally increased more than the research related to water in the same period. **Figure 1** shows that the publications registered in Web of Science that included in the title the word "seawater" increased from 226 to 753 from 2000 to 2016. **Figure 1** also shows the evolution of publications that include in their title seawater and are related to mining.

The areas in which it is published on seawater have changed in recent years. During the period 1996–2005, the areas with the most publications were chemistry analytical (339), water resources (302), and oceanography (300). On the other hand, during the period 2006–2015, the areas were water resources (731), environmental science (692), and chemical engineering (692). This change reflects a greater interest in seawater as a water resource (see **Figure 2**).

The shortage of fresh water in arid areas is an economic, environmental, and social problem. Specifically, demand for seawater for mining requires energy for desalination and transport from the coast to high-altitude areas. Then, the use of seawater generates energy demand, another scarce resource. This increased consumption of energy can generate more pollution, as is the emission of greenhouse gases. Thus, besides the possible direct environmental effects of using seawater, indirect effects are also generated. Moreover, it is clear that the use of seawater is usually more expensive than other sources. Seawater can be used without desalting, but this requires that the process must be adapted to new conditions. Among these, new conditions are possible interactions of elements dissolved in seawater with minerals, chemicals,

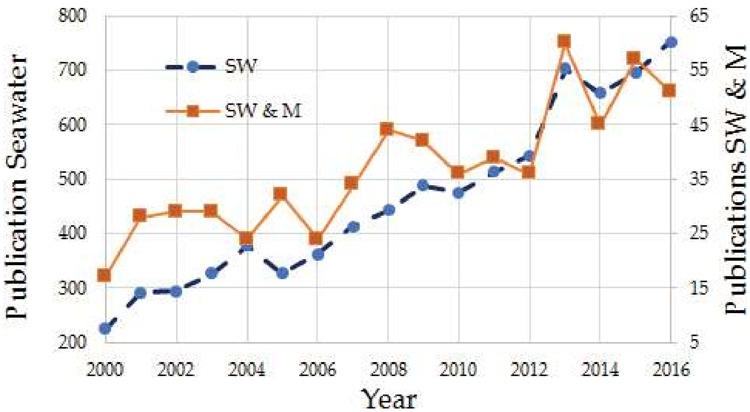

Figure 1. Publications in Web of Science that include in the title seawater (SW) and seawater related to mining (SW & M).

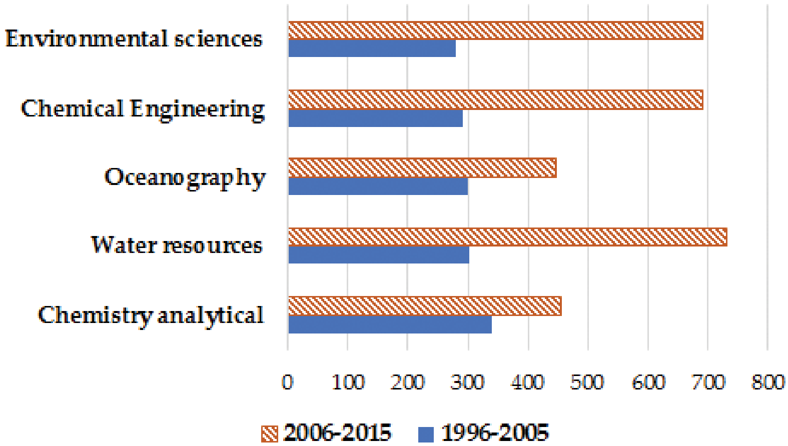

Figure 2. Areas of publications in Web of Science that include in the title seawater.

and materials used in the equipment. Then, new technologies are needed to adapt traditional processes to seawater without desalination.

Chile main economic activity, based on production and income, is mining. The main ore deposits are located in the regions that are part of the Atacama Desert. These regions are rich in copper, gold, molybdenum, silver, iron, nitrate, boron, iodine, lithium, potassium, and other resources. Chile's abundance of mineral resources is remarkable: Its reserves constitute 6.7% of the world's gold, 12.1% of the molybdenum, 13.3% of the silver, 27.7% of the copper, 53% of the rhenium, 57.9% of the lithium carbonate, 60.8% of the iodine, and 100% of the natural nitrates [1]. In addition to its abundant resources, Chile's mining industry is boosted by several other natural, technological, and administrative advantages as such mineral deposits in the vicinity of many seaports, the desert setting surrounding the large deposits facilitates land claiming, exploration, and exploitation, large deposits enable the use of massive and low-cost technologies, among others. However, Chilean mining also faces major challenges, such as the lowering of the grades in its deposits, high energy costs, and scarce-water resources. In 1992, 21% of the world copper production was made from minerals with better grades than Chilean minerals. That percentage has been increasing, and in 2010, 35% of the world production was with better grades than the Chilean ones. It is projected that by 2020 this percentage will be 43% [2]. This means, among other things, that more energy and water resources will be required per ton of copper produced. Chile has one of the highest electricity rates among the mining countries [2], only surpassed by the Congo. Also, and as we will see later, water resources are very scarce, and the use of seawater has a high cost due to the difference in altitude between the coast and the location of mining operations.

Figure 3 shows a scheme of the region of Antofagasta, the main mining region of Chile. After a narrow plain on the coast, the mountain of the coast is situated, where copper mines are found, most of them of medium or small size. These mountains usually have an altitude of about 800 m.a.s.l. Then there is the Atacama Desert where the main mines are nitrates

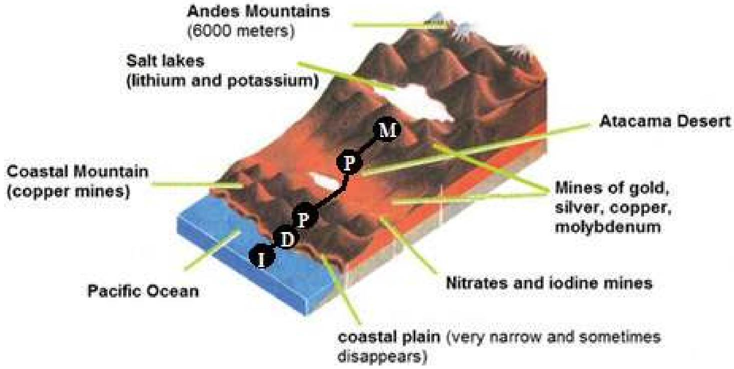

Figure 3. Geographical scheme of the Antofagasta region, mining activities, and seawater catchment system. (I: Intake, D: desalination plant, P: pumping system, M: mine).

and iodine, but where copper and molybdenum mines are also observed. In the Domeyko and Andes mountains are the largest copper mines, along with deposits of gold, silver, and molybdenum. These mountains have altitudes between the 2000 and 6000 m.a.s.l. To supply water from the ocean, it is necessary to have an intake system, seawater pretreatment/desalination, and a pumping system to reach the mining plant located near the mines.

This chapter describes the current use of seawater, with and without desalting, in the mining sector in Chile, as well as its future projection. Section 2 gives a description of the current seawater consumption, the desalination systems, mining operations currently using seawater and new projects, current water distribution systems, seawater applications in hydrometallurgy and minerals concentration, their environmental impacts, difficulties in adapting processes in case of use of seawater without desalination. Section 3 gives innovative solutions for sustainable use of seawater, including integrated seawater distribution systems, seawater biodesalination, partial desalination using carbon dioxide, adaptation of process to the use of seawater without desalination, and uses of discard brines from reverse osmosis plants. Finally, a section of conclusions and comments is included.

2. Current use of seawater in mining

The use of seawater is not new and deposits of copper, zinc, uranium, and iodine have been processed using this water resource without desalination. For example, the El Boleo project processes copper, cobalt, zinc, and manganese minerals (by leaching) in Mexico, and Sierra Gorda SCM processes copper and molybdenum (by flotation) in Chile. Some operations using seawater have closed down, for example, Black Angel (Greenland) floated a lead-zinc ore, and Minera Michilla (Chile) was leaching a sulfurous copper ore. Currently, in Chile, several mining companies use seawater, with and without desalination, let's see the current situation.

Copper mining, Chile&s main water-consuming in mining, consumes 15.4 m^3/s of fresh water. Of this fresh water, 85% is of continental origin, which includes surface water, groundwater, and water purchased from third parties (see **Figure 4**). The remaining 15% corresponds to seawater, which includes raw seawater and desalinated seawater. This fresh water is used in the mine (0.6 m^3/s), hydrometallurgical processes (2.2 m^3/s), in the concentrator (11.1 m^3/s), smelter and refinery (0.5 m^3/s), and other uses (0.8 m^3/s). The fresh water only corresponds to 28.6% of the water used in the processes because 72.4% (40.4 m^3/s) corresponds to recirculated water. These values were calculated based on information provided by Chilean Copper Commission (COCHILCO) [3] for the use of continental waters and assuming that desalinated seawater is used in the same proportion in the mining areas as continental water and that raw seawater is used 100% in the concentrator.

Not all of the water is recycled because there are losses by evaporation in the leaching process and in the storage ponds, losses in the tailings ponds, filtrations, infiltrations, among others. However, efforts are made to reduce water losses, for example, by covering the ponds

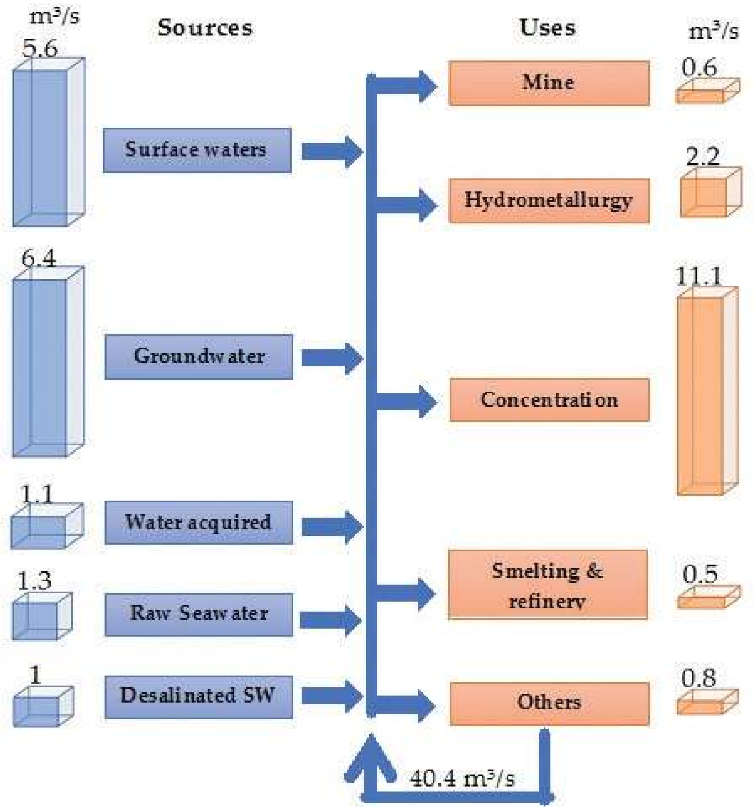

Figure 4. Sources and uses of fresh water in the copper industry in Chile based on COCHILCO studies [3].

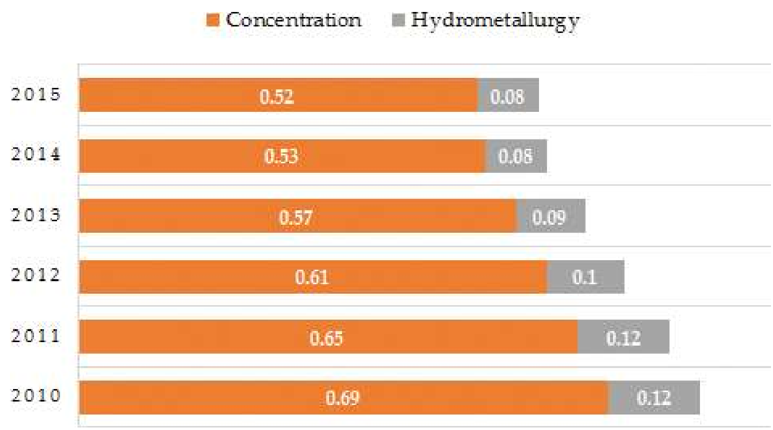

Figure 5. Water consumption in cubic meters per ton of treated ore [3].

and improving the thickening systems. In fact, water consumption per ton of ore has been reduced by 25.9%, from 0.81 m^3/t in 2010 to 0.60 m^3/t in 2015. **Figure 5** shows the consumption of the concentrator and in hydrometallurgy. It can be observed that the consumption of the concentrator plant is 6.5 times the consumption in hydrometallurgy per ton of mineral. Unfortunately, the main mineral of copper and of which there are greater reserves in the world, chalcopyrite, is preferably processed by the concentration of minerals.

2.1. Consumption of seawater and its projections

Given the depletion of continental water sources, new operations or expansion of new operations in water-scarce areas should use seawater. In fact, the use of surface water decreased from 5.9 to 5.6 m^3/s from 2013 to 2015, while groundwater increased slightly from 6.2 to 6.4 m^3/s. However, the use of seawater in the same period increased from 1.3 to 2.3 m^3/s. **Figure 6** shows the evolution of the consumption of seawater, with or without desalination, from 2010 to 2015 observing a significant and sustained increase. There are currently 10 desalination plants of mining companies that produce between 5 (Minera Pampa Camarones) and 500 L/s (BHP Billiton and Lundin Mining have plants of similar capacity). On the other hand, seven mining operations use raw seawater with capacities of between 5 (Compañia Minera Tocopilla) and 1500 L/s (Antofagasta Minerals). Currently, 15 projects for the installation of new desalination plants are in different stages. Stand out the projects of Coloso BHP Billiton plant (at start-up stage) for 3200 L/s and Radomiro Tomic CODELCO for 1900 L/s, which will significantly increase the use of seawater. Additionally, four projects will use raw seawater with an approximate consumption of 1100 L/s.

Currently, each mining plant establishes its water supply system. This means that there are currently 17 water pumping systems (10 of desalinated seawater and 7 of raw seawater) from the coast to the mountains and that these pumping systems will increase to 36 if each project materializes.

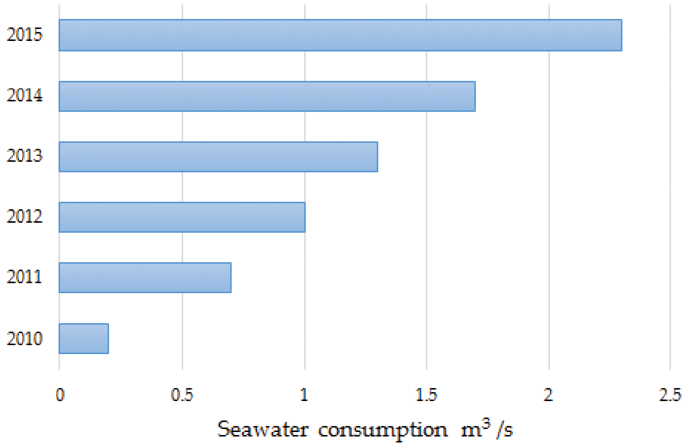

Figure 6. Seawater consumption in mining in Chile [3].

2.2. Reverse osmosis desalination versus raw seawater

The use of raw seawater has advantages and disadvantages. In the treatment of some minerals, its effect is positive favoring the extraction of valuable species, while in other cases, its effect is contrary. This is generated because seawater presents numerous species that interact with the process. As the desalination is not included, there are no high energy costs and their environmental effects are lower. The presence of chloride ions causes corrosion problems in equipment that is in contact with seawater.

The use of desalinated seawater also has advantages and disadvantages. How this water does not contain dissolved species does not observe positive or negative effects in comparison to other process water. Although the process of desalination by reverse osmosis, the technology used in all projects in Chile is the most energy-efficient technology, it requires a high energy consumption. This current energy consumption is not too far from the theoretical minimum energy required for desalination [4]. Electricity generation in northern Chile is based on fossil fuels, which is why desalination generates negative environmental effects. Recently, some solar-based electricity production capacities have been urged, but they are still insufficient. In addition, desalination by reverse osmosis generates a discharge brine, with a salinity of approximately twice the seawater. This discharge brine and the chemicals used in pretreatment and membrane-cleaning can generate negative effects to the environment [4]. Pure desalinated seawater is highly acidic and is thus corrosive, so it has to be posttreated to adjust for pH, hardness, and alkalinity before being piped [5].

It has been demonstrated in practice that both types of water, raw and desalinated seawater, can be applied to mining processes. The decision depends on the characteristics of the ore, the associated costs, and the capabilities or possibilities of adapting the mining operation to the use of raw seawater. **Figure 7** shows that the consumption of both types of waters has been increasing since 2010.

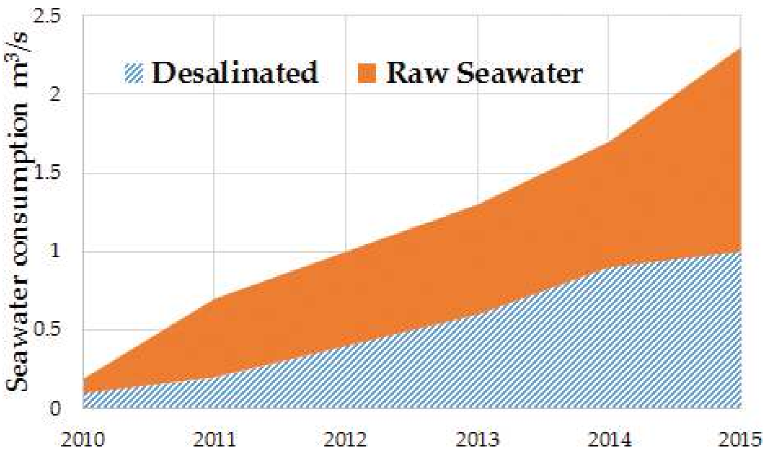

Figure 7. Consumption of raw and desalinated seawater in mining activities in Chile [3].

2.3. Seawater distribution networks

The main mining activities in Chile are located over 1000 m.a.s.l., which creates a great challenge for the industry. **Figure 8** shows the costs of using desalinated water in different countries. It can be observed that the costs of desalination are similar between countries, and this is around 1.5 USD/m^3. However, the operating and capital costs of transporting water in Chile are higher than in other countries. In fact, the costs of transporting can be more than three times the costs of desalination. This is explained by the fact that the altitude of the mining deposits in Chile is higher than in other countries, as shown in **Figure 9**. The operational costs of transportation are mostly the costs of energy consumption associated with water pumping.

As indicated above, currently each mining plant establishes its water supply system. Currently, there are 17 water pumping systems from the coast to the mountains, and these figures can increase over 100% if the new projects materialize. The current strategy is not sustainable in the future, especially for medium and small-scale mining.

2.4. Effect of raw seawater in mining operations

The effects of using raw seawater in mining operations are diverse. Seawater contains dissolved ions that interact with minerals producing positive and negative effects on operations. The major ions dissolved in seawater are sodium and chloride, where the sodium effect is not significant, but the chloride ion helps to improve the leaching of some copper sulfide minerals [6, 7] and helps the stability of the bubbles in the flotation of copper sulfide minerals [8, 9]. Thus, in principle, the chloride and sodium ion may not be withdrawn from seawater. It has been observed that the presence of magnesium and calcium ions produce problems in the molybdenite flotation of copper-molybdenum ores [10]. These problems are due to the precipitation of these ions under the operating conditions of the flotation. Also, it has been observed that by removing or reducing the concentration of magnesium and calcium, the

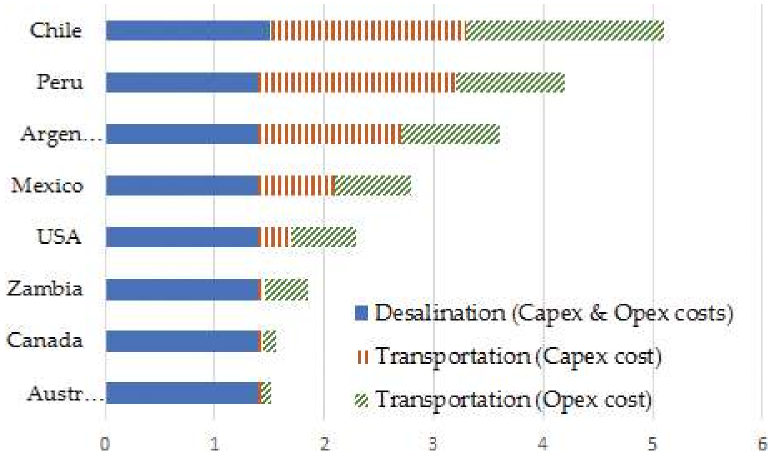

Figure 8. Desalination and transportation costs in USD/m^3 [4].

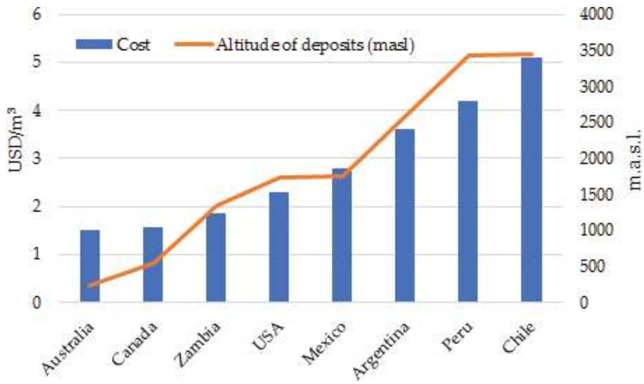

Figure 9. Transportation cost and altitude of mineral deposits [4].

negative effects of seawater in flotation are overcome. In simple terms, it can be said that the partial desalination of the magnesium and calcium ions is enough to use seawater in operations of concentration (flotation) of minerals. It is necessary to remember that the operation that consumes the most water is the concentrator.

Seawater also has gases dissolved by its contact with the atmosphere. The main gases are oxygen, nitrogen, and carbon dioxide, and the latter reacting in aqueous media generating bicarbonate and carbonate ions. The presence of oxygen in all waters produces corrosion, and in the case of seawater, its effect should be lower because the solubility of oxygen decreases as salinity increases. However, the presence of chloride ions generates a more corrosive environment, reason why measures must be adapted to avoid the corrosion of the equipment.

Seawater has also been used in the leaching of caliche minerals [11]. Caliche is a mineral rich in soluble species such as salts of chlorides, nitrates, and sulfates of sodium, magnesium, and potassium, as well as iodine salts. The main products are salts of nitrate and iodine. The use of seawater in the leaching of these minerals does not present great differences compared to non brackish waters because the mineral is rich in salts and the solutions recirculated to the process contain dissolved ions in a much greater concentration than the seawater.

3. Innovative solutions for sustainable use of seawater

This section presents examples of innovative solutions to the problems of the use of seawater in mining processes. These solutions have been developed through the project "Atacama seawater: process integration for water and energy saving." All these research seek to use seawater in a more sustainable way, especially reducing the environmental impact of the use of seawater in mining.

3.1. Integrated seawater distribution networks

As noted above, mining companies have begun to use desalinated seawater as an alternative to supplying part or all of their demands. However, these efforts have been carried out independently, that is, each user or mining company has installed its desalinated water production and distribution system, without considering the possibility of designing an integrated production and distribution system. Currently, the region of Antofagasta has more than 40 mining industries in operation, which are located, regarding distance, from a few kilometers of the coast to about 200 km. However, the most important thing to consider is that these industrial plants can be found between 600 and 4000 m above sea level, due to the complex topographical profiles existing in the region. This location becomes a problem if one considers using desalinated seawater to supply its production systems, significantly increasing the engineering challenges in the design of the water production and distribution system for each mining plant.

Due to the complex topography of the region, the desalinated water supply systems that have been designed and are currently operating have faced several economic, technical, and environmental challenges, such as the high energy requirement of the desalination plant and the water supply system. The desalinated water delivery system consists of a pipeline, a series of reservoirs, pumps, among other hydraulic compounds. The fundamental purpose of the system is to provide a safe supply of freshwater with a certain established quality. The design of the system is basically determined by the distances between the coast and the point of use of the water, the difference in elevation between these same points and the characteristics of the soils where the project will be carried out.

In northern Chile, the capital and operational costs of the desalinated water delivery system are the highest in the entire desalination project. The data provided by Guerra et al. [12] indicate that when mining plants are under 1000 m above sea level, the capital costs of the desalination plant are similar to the capital costs of the desalinated water delivery system.

In contrast, when the mining operation is above 3500 m.a.s.l., the capital costs of the delivery system can be two to five times more than the capital costs of the desalination plant. These costs are increased mainly by the greater number of pumping stations needed to boost the desalinated water to the required point, that is, the costs are a function of the location height of the mining plant. **Table 1** shows the capital and operating costs of six mining projects in northern Chile.

Recently [13, 14], a procedure has been developed to design an integrated desalinated water production and distribution system for the Antofagasta region. The purpose of an integrated water distribution system is to supply different users with different requirements in a more efficient way, both economically and environmentally. This system can be represented by an interconnected network of pipes, pumps, valves, among other hydraulic elements. The procedure developed is based on a mathematical model that represents a set of alternatives, whose solution is obtained looking for the optimal solution from the point of view of cost. This procedure is not described here, but a case study is used to describe the results obtained.

The case study carried out for the Antofagasta region consisted of the integration of six mining sites in the northern region of the Antofagasta region (between latitudes 21° 30'S and 23° 1'S), which were located using geographic information software, Google Earth Pro 7.1 (**Figure 10**). The three indicators shown in **Figure 10** represent the following: the indicator PO represents the reverse osmosis plants, the indicator EB to the pumping stations, and the indicator PM to the mining plants. For each mining plant, different requirements of desalinated water, elevation above sea level and distance from the coast were considered. The desalinated water requirements considered vary between 100 and 400 L/s. The distances of each of these operations toward the coast were defined between 60 and 195 km, while elevations were between 1700 and 3800 m.a.s.l. A maximum of six reverse osmosis plants was considered since the integrated system was born from the integration of six independent systems. Each desalination plant may have sufficient capacity to meet the desalinated water requirements of all the mining plants considered in the study. The drive system consisted of 25 pumping stations. Also, it was considered that the maximum elevation difference to

Capacity RO plant (L/s)	Elevation (m.a.s.l.)	Capital cost (MUS$/year)		Operational cost (MUS$/year)	
		RO plant	Water delivery system	RO plant	Water delivery systems
1000	4150	264.4	428.3	22.4	65
550	4400	190.8	412.4	16.8	47.5
180	830	147.2	328.7	13.2	35.9
700	3650	27.9	29.1	3.24	1.68
500	500	63.4	163.4	11.6	16.9
271	4100	42.8	48.9	6.68	5.16

Table 1. Capital and operational costs of reverse osmosis (RO) desalination projects developed in northern Chile [11].

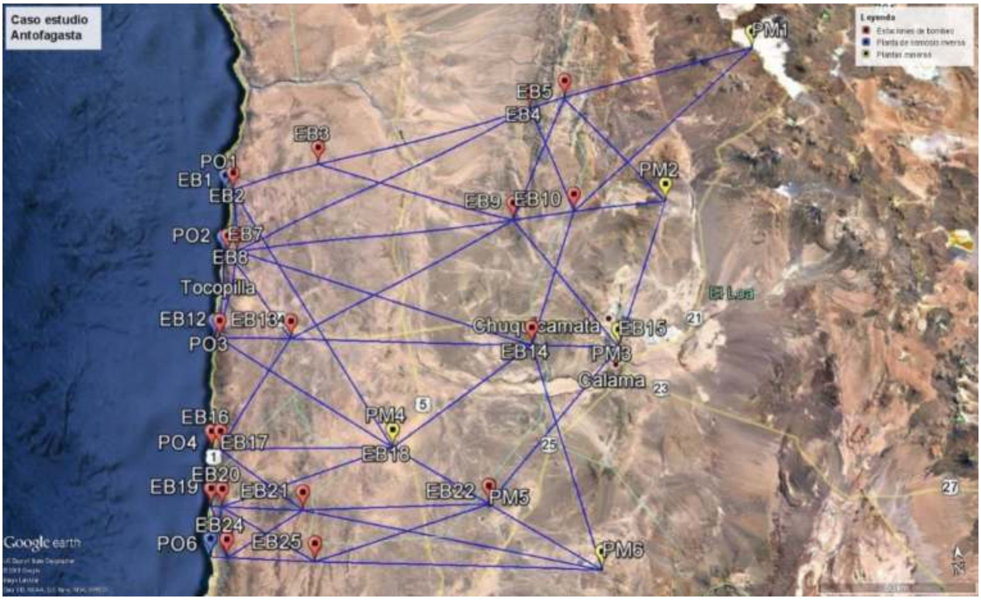

Figure 10. A case study of an integrated desalinated water supply system for six mining plants in the Antofagasta region. PO indicator: reverse osmosis plants; EB indicator: pumping stations; and PM indicator: mining plants [14].

connect two nodes with one pipe was 700 m. Finally, to evaluate the design, five types of pipe diameters were considered that fluctuated between 0.7 and 1.1 m. The investment years considered for the project were 25 years.

The problem was modeled and solved in a commercial optimization software. The results obtained indicated that the optimum model should be constituted by a reverse osmosis plant and seven pumping stations as shown in **Figure 11**.

Alternative 1 represents the current strategy of the mining companies, that is, the use of independent supply systems. Alternative 2 represents the proposed solution. In alternative 1, six reverse osmosis plants must be installed to satisfy the water requirements of each mining plant independently. Alternative 2 indicates the need for only one reverse osmosis plant and fewer pumping stations than alternative 1. Also, the productive capacity of the reverse osmosis plant of alternative 2 is greater than any other reverse osmosis plant considered in alternative 1. On the other hand, the unit cost of production of the reverse osmosis plant is lower due to economies of scale.

The results indicate that the costs of reverse osmosis plants occupy between 29 and 32% of total project costs, pumping stations between 40 and 52%, and pipes between 20 and 27%. The results show that alternative 2 involves a lower cost in the installation of the reverse osmosis plant and pipes. On the other hand, the costs of pumping stations increase slightly relative to alternative 1. In **Figure 11**, alternative 2, it can be seen that the production flow of desalinated water is separated into two streams after supplying the first mining plant. This is

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Figure 11. Optimum proposed model of an integrated desalinated water supply system for six mining plants in the Antofagasta region. PO indicator: reverse osmosis plants; EB indicator: pumping stations; and PM indicator: mining plants [14].

mainly because the proposed strategy has a main objective to reduce the costs of the pumping stations, which are directly proportional to the capacity (size) of each station, which is related to the flow driven.

Based on the results obtained, it was observed that there is a relationship between the three considered costs, such as costs of reverse osmosis plants, costs of pumping stations, and pipe costs. These results allow us to propose that an integrated desalinated water distribution system design, which satisfies the requirements of more than one user, is a valid alternative that will also allow decreasing the costs of production of desalinated water to each interested user.

3.2. Biodesalination of seawater

As indicated above, the main problems in using seawater in flotation processes of copper-molybdenum minerals are the presence of magnesium and calcium ions. For that reason, it seems reasonable to look for processes that are capable of eliminating or reducing the concentration of these species selectively. These new processes must be economically and environmentally superior to reverse osmosis plants. The selective removal of these ions, also, allows maintaining the species that are harmless or help to the flotation process as is the case of the sodium and chloride ions, respectively. A biotechnological alternative for the selective removal of these secondary ions from seawater is the application of bacteria that are capable of inducing the formation of insoluble crystals with these ions through a phenomenon known as biomineralization or microbiological precipitation of carbonates. In this way, the calcium and magnesium ions are removed at a lower cost and in an environmentally friendly way.

The concept of biomineralization or microbiological precipitation of carbonates is defined as the process involving the formation of minerals by living organisms as a result of cellular activity that promotes the physicochemical conditions required for the formation and growth of the biominerals is carried. This process is mainly generated from bacterial activity, which is able to induce the precipitation of minerals by processes classified as biologically controlled mineralization and biologically induced mineralization [15].

In biologically induced mineralization, minerals are precipitated by the interaction between the environment and its chemical changes and the biological activity resulting from bacterial metabolic activity [15, 16]. In this type of biomineralization, the biominerals are secreted due to the metabolism of the microorganisms, and the system has very little control over the deposited minerals. There are a large number of bacteria capable of inducing extracellular precipitation from a wide range of biologically induced minerals, involving the geochemical activity responsible for mineral deposits in terrestrial evolution.

The best-studied mechanism for the precipitation of calcium carbonate is through the ureolytic pathway, in which the bacteria degrade urea by the intracellular enzyme urease, producing HCO_3^- and NH_3. The latter is converted to NH_4^+, alkalinizing the medium, and HCO_3^- is converted to CO_3^{2-} [17]. When the calcium ion is present, and the supersaturation of calcite occurs, the precipitation of calcium carbonate is induced.

Silva-Castro et al. [18] demonstrated the precipitation of calcium carbonate in seawater and brines from desalination plants, using Bacillus and Virgibacillus bacteria isolated from saline environments, confirming that these species can precipitate calcium carbonate when grown in culture media supplemented with organic matter. The precipitation of magnesium from seawater by the use of ureolytic halotolerant bacteria has not been described. However, the precipitation of struvite by chemical crystallization using the NH_4^+/PO_4^{2-} ratios in solution was studied [19], concluding that the use of seawater as a source of Mg for phosphate precipitation is feasible, mainly due to the high concentration of magnesium available (about 1.29 g/kg).

These studies were the basis for studying the feasibility of using ureolytic bacteria and their metabolic products as a possible technology for the removal of Mg and Ca from seawater. Considering the characteristics of the Salar de Atacama (it is the oldest, dry, and hot of the whole planet [20]), bioprospections were realized for the search, isolation, and selection of bacteria with ureolytic activity able to tolerate the salinities present in seawater for the biomineralization of calcium and magnesium. A total of 213 bacteria were isolated from these samples, of which 40 were found to have urease activity and are halotolerant and/or halophilic, capable of growing in seawater [21–23]. The phylogenetic identification of the bacteria with urease activity allowed to determine that they belong to different genera, being the most abundant the bacteria of the genus Bacillus with a representation percentage of 42%. The advantage of using isolated bacteria in the study site means the use of bacteria native to the environment that pose no health risks.

Recent laboratory-scale studies have shown that two of the selected bacteria can remove calcium ions by 100% and magnesium ions present in seawater by 40% in a period of 7 days, inducing the formation of Crystals composed of ~31% monohydrocalcite, ~28% struvite ($MgNH_4PO_4 \cdot 6H_2O$), ~33% halite (NaCl) and ~8% anhydrite ($CaSO_4$) (**Figure 12**). Further studies are underway to establish a process that is capable of partially desalinating seawater.

3.3. Partial desalination using CO_2

A second alternative for the selective removal of Mg and Ca from seawater is precipitation using some alkalinizing agent and carbon dioxide (CO_2 (g)) [25]. This emerging technology could be a potential process to supply the water quality demanded by the process of flotation of Cu and Mo sulfide minerals and at the same time reduce the greenhouse effect generated by the emission of CO_2 (g) and avoid the discharge of brines of reverse osmosis plants to the sea. It is necessary to remember that thermoelectric plants mainly provide the energy used in the north of Chile. They use nonrenewable fossil fuel such as coal. Carbonization has led to an increase in CO_2 (g) emissions into the atmosphere.

When CO_2 (g) is solubilized in seawater, several reactions are generated that eventually generate bicarbonate ion (HCO_3^-) and ion carbonate (CO_3^{2-}). Based on the interactions that occur in the carbonate system and the ions present in seawater, an additional source of CO_2 (g) on seawater promotes a greater formation of CO_3^{2-}, further inducing the precipitation of calcium carbonate ($CaCO_3$), and magnesium carbonate ($MgCO_3$), among other species.

In this work, the removal of calcium and magnesium from seawater of the San Jorge Bay in Antofagasta using NaOH and CO_2 was studied. The experimental tests were performed with NaOH as alkaline reagents (to maintain constant pH) and different doses of CO_2. The tests were carried out at pH 10 and 10.5, with NaOH, without CO_2 and then with injections of 70 and 210 mL of CO_2. The amounts of Ca and Mg, which precipitated under these conditions, were calculated from the difference between the concentrations before and after the addition

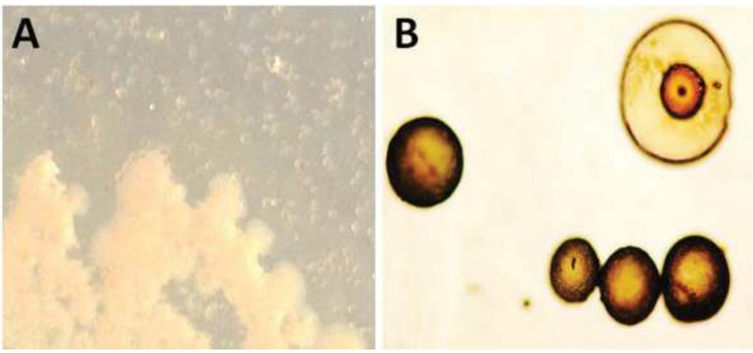

Figure 12. Precipitation of calcium carbonate by strain LN8B. (A) Crystals and colonies in the presence of urea and calcium chloride; (B) microphotography of crystals on day 4 of culture [24].

of NaOH and CO_2. Then, the Ca and Mg concentrations were determined by atomic absorption spectrophotometry.

It was observed that the removal of Ca and Mg increased as CO_2 was added, reaching 31.4 and 70.0%, respectively at pH 10.5 and 210 mL of CO_2. These values are greater than the removal when using only NaOH (without CO_2) corresponding to 11.8 and 13.8% for Ca and Mg, respectively. Subsequent studies using NaOH, Na_2CO_3, and combinations of these alkaline agents and CO_2 injection have shown that this emerging technology has significant economic and environmental advantages compared to the use of reverse osmosis.

3.4. Potential uses for discarding brines from reverse osmosis plants

One way to reduce the environmental impacts of desalination plants by reverse osmosis is to look for uses to the discard brines that they generate. These brines would have a lower cost than seawater since they have already been taken and pretreated. Currently, a very small fraction is used to irrigate roads to reduce dust in mining operations. One possible use is the leaching of caliche minerals.

As indicated above, caliche is a mineral conformation whose composition rich in highly water soluble species makes it a commercially exploitable source of nitrates and iodine. These products have a wide range of applications, such as the use of nitrates for the production of high-performance fertilizers, as well as the use of iodine as an additive in industrial plants and an input in medical products [26]. The processing of caliche for the production of nitrate and iodine salts consists of four fundamental stages: (1) extraction of the mineral, (2) leaching, (3) extraction of iodine, and (4) evaporation and crystallization of the nitrate.

In current reverse osmosis plants, efficiencies of 40–50% are handled, which means that to produce a cubic meter of desalinated water, a similar amount of solution is produced with twice the concentration of salts than the incoming seawater. **Table 2** shows the composition of the seawater and the discard brine of a plant in the north of Chile [27].

Recently, a caliche mineral was leached using seawater (note that seawater is currently used in some plants [26]) and discard brine from a local desalination plant [28]. The leaching was carried out for 22 days in columns of 1.0 m of effective height and 20 cm of internal diameter, and 3 different irrigation rates were used: 4, 6, and 8 $L/h/m^2$. The liquid samples from the percolates were taken every 12 h for the first 5 days, and after that the sampling was done every 24 h. Samples of caliche and leftover material were also taken. The ions considered throughout this study, both liquids and solids were: nitrate, iodate, chloride, sulfate, perchlorate, boron, sodium, potassium, magnesium, and calcium.

To evaluate the performance of the leaching, the concentration profiles (concentration versus leachate volume) were compared. Some species dissolve rapidly during leaching, such as nitrate, sodium, perchlorate, and iodine, while others do it more slowly such as sulfate, potassium, magnesium, and boron. The differences between the columns watered with seawater and discard brine are small for the first part of the leaching. Afterward, some differences were

Iones	Unidad	Seawater	Discard brine
Chloride	kg/m^3	18.4	36.0
Sodium	kg/m^3	11.1	25.2
Sulfate	kg/m^3	2.8	5.4
Magnesium	kg/m^3	1.4	2.9
Potassium	kg/m^3	0.6	2.5
Calcium	kg/m^3	0.5	0.9
Nitrate	kg/m^3	0.3	0.4
Borate	g/m^3	10	30
Yodate	g/m^3	<10	10
Perchlorate	g/m^3	<10	10
Density	kg/m^3	1020	1040

Table 2. Principal dissolved salts in seawater and reverse osmosis discard brine [27].

observed because once the ore is depleted, the percolates take the initial concentration of the seawater or the discarding brine.

Regarding the extraction profiles, no substantial differences were found in the recoveries between leaching using seawater and desalination plant brine, especially in the species of commercial interest: nitrate and iodine. Their recoveries were similar and reached high values (greater than 97%). These results support the conclusion that it is technically feasible to employ reverse osmosis brines for caliche leaching.

An important point to note is that the use of reverse osmosis brine for caliche leaching does not imply replacing the infrastructure of pipes and other equipment at the mine site, since nitrate operations handle even more concentrated solutions. If the brines are transported instead of seawater from the coast to the mine, a change of piping would not be required either, since the corrosive activity of the brines could be less than that of seawater because the solubility of the oxygen decreases as the salinity increases.

4. Conclusions and comments

The use of seawater in mining generates a series of challenges ranging from the same take of the seawater until its use in the mining plant. Its use must consider economic, environmental, and social aspects. In the Atacama Seawater project, we have taken part of these challenges, some described in this chapter. The search for solutions to these challenges has led us to seek answers that are innovative. Without a doubt, there are still many steps to be taken to materialize these proposals, and therefore further research, developments, and innovations are necessary.

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Author details

Edelmira D. Gálvez[1]* and Luis A. Cisternas[2]*

*Address all correspondence to: egalvez@ucn.cl and Luis.Cisternas@uantof.cl

1 Department of Mines and Metallurgical Engineering, Universidad Católica del Norte, Chile

2 Department of Mineral Process and Chemical Engineering, Universidad de Antofagasta, Chile

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