minerals

Review

Copper Bioleaching in Chile

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Abstract: Chile has a great tradition of producing and exporting copper. Over the last several decades, it has become the first producer on an international level. Its copper reserves are also the most important on the planet. However, after years of mineral exploitation, the ease of extracting copper oxides and ore copper content has diminished. To keep the production level high, the introduction of new technologies has become necessary. One that has been successful is bioleaching. Chile had the first commercial operation in the world exclusively via bioleaching copper sulfides. Nowadays, all bioleaching operations run in the country contribute to an estimated 10% of total copper production. This article presents antecedents that have contributed to the development of copper bioleaching in Chile.

Keywords: bioleaching; copper production; large scale; sulfide minerals

1. Introduction

Chile has important mineral wealth, where copper stands among the most important. Back in its history, the Spanish conquerers realized the potential of Chile as a mining territory, although at that time they were mostly focused on the recovery of gold and silver. During the 17th and 18th centuries, copper exploitation was a small industry that became important at the beginning of the 19th century after the independence of the country. However, at the end of that century, copper production sharply decreased especially because minerals with high copper content became scarce, and the investment of the mining sector focused on nitrate salt production as a natural fertilizer. At the beginning of the 20th century, this situation changed mainly because foreign companies having the adequate technology to recover the metal present at lower concentrations made investments and initiated its exploitation. Two of the most emblematic mines in Chile were established at that time: El Teniente, owned by the Braden Copper Company in 1904, later controlled by the Kennecott Corporation, and Chuquicamata, built by the Chile Exploration Company in 1910, later sold to the Anaconda Copper Company.

Two important steps given by the country were the "Chilenization" of the copper industry in 1966, meaning that the state of Chile made the necessary investments in order to become the owner of 51% of each one of the most important mines in the country. Later in 1971, the state of Chile took complete control of the mines partially owned at that time by foreign investors. Any further exploitation of new mines based on private investors had to be authorized by state law. As a consequence, in 1976, the Corporación Nacional del Cobre de Chile (CODELCO) was created as a state enterprise gathering the principal mines in one huge corporation.

In terms of copper production, during the period of colonization, the amount of copper produced is estimated to be between 1500 and 2000 tonnes per year. Most of that copper remained in Chile, destined to make decorative objects, different utensils and tools, coins, pieces of artillery, *etc*. Only approximately one third was exported annually.

The situation changed in an ostensible manner in the 19th century, when the copper was demanded by a great variety of technological applications derived from the European industrial revolution. It is estimated that, between 1820 and 1900, Chile produced 2 million tonnes of copper, being, for a time, the number one producer and exporter of the world. The peak production occurred in 1876 at 52,308 tonnes of copper, 30% of the world's production. Toward the end of the century, this position fell down to 9.7% in 1890 and to just 5.5% in 1900 [1–3].

The definitive takeoff of copper mining in Chile started at the beginning of the 20th century, along with the exploitation of new, large mineral sites. Since then, the annual production of copper has increased to occupy the primary producer of copper in the world, with a volume equivalent to approximately one third of the world's production, as is depicted in Table 1. The highest participation of Chile in world copper production so far was in 2004 at 36.9%.

Table 1. World and Chilean copper mine production (thousands tonnes/year) [1,4–6].

Year	Chile	World	Chilean Production
	thousands tonnes/year		%
1900	27.7	493.9	5.3
1910	38.2	880.5	5.6
1918	106.8	1416.1	7.5
1929	320.6	1943.0	16.5
1950	362.9	2542.2	14.4
1960	531.9	4236.7	12.6
1970	691.6	6350.6	10.9
1980	1067.9	7713.9	13.8
1990	1588.4	8956.5	17.7
2000	4602.0	13,246.5	34.7
2010	5418.9	16,114.3	33.6
2014	5749.6	18,515.6	31.1

The principal mines operating nowadays in Chile and their copper production in 2014 are listed in Tables 2 and 3 corresponding to those owned by CODELCO and private investors, respectively.

Table 2. Copper mine production by Corporación Nacional del Cobre (CODELCO) in 2014 (thousands tonnes/year) [4].

Mine	Copper Production
Chuquicamata	340.4
El Teniente	455.5
Radomiro Tomic	327.3
Ministro Hales	141.2
Salvador	54.0
Andina	232.4
Gaby	121.0

The copper production in Chile is based mostly on the exploitation of ores containing copper sulfides, with chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), covellite (CuS), bornite (Cu_3FeS_3), enargite (Cu_3AsS_4), and tennantite (Cu_3AsS_3) being the most important. Through the years of exploitation of the copper in Chile, the ore mineralogical composition has changed. In the past, the oxides, easy to produce, were abundant, and the copper content was over 5%. Nowadays, the copper oxides have become scarce; practically speaking, the only sources of copper are sulfides, and its content has diminished down to approximately 1%. In accordance with this change, the reserves of copper in Chile consist mainly of chalcopyrite, which in 2012 was estimated to be in 190 millions of tonnes of copper, representing approximately 30% of the world's copper reserves [7].

Table 3. Copper mine production in Chile by private owners in 2014 (thousands tonnes/year) [4].

Mine	Copper Production
Escondida	1165.4
Collahuasi	470.4
Los Pelambres	404.6
Anglo American Sur	436.9
El Abra	166.4
Candelaria	134.7
Anglo American Norte	104.2
Zaldívar	100.6
Cerro Colorado	79.6
El Tesoro	93.8
Quebrada Blanca	48.1
Lomas Bayas	66.4
Michilla	47.0
Spence	176.1
Esperanza	180.7
Caserones	44.6
Sierra Gorda	12.7
Others	345.6

2. Bioleaching of Sulfide Minerals

2.1. Bioleaching Process

There is evidence that ancient people learned how to recover naturally bioleached copper. One example is found at the time of the Roman Empire or in Rio Tinto, Spain, back in the 18th century, where there is evidence that copper was recovered from acidic waters. However, the development of this biotechnology actually started in circa 1950, once bacteria involved in the leaching of copper were isolated and characterized [8–10]. This basic knowledge allowed the initiation of understanding of the relation between this special microbial activity and copper dissolution, and its potential as an alternative technology for copper recovery.

In brief, bioleaching is the oxidative solubilization of sulfide mineral mediated by the action of microorganisms. Most commonly used acidophilic bioleaching microorganisms are chemolithoautotrophic and thus use inorganic energy and carbon sources. They use ferrous iron and/or reduced sulfur compounds as an energy source, and chemical elements commonly found in ores, particularly in copper ores. The ferric ion generated by microbial action is a strong oxidant of the copper sulfides, liberating the metal into solution. The reduced sulfur compounds generated during ferric attacks are oxidized to sulfuric acid by microorganisms maintaining a low pH, which is essential for acidophiles and ferric iron solubility. Closing the cycle, the reduced iron generated during mineral attacks is re-oxidized by the microorganisms. Two ways of oxidation of the mineral sulfide have been proposed and depend upon its composition [11–14]. The so-called thiosulfate pathway oxidizes species like pyrite, molybdenite, and tungstenite, while sphalerite, chalcopyrite, arsenopyrite, and galena are oxidized via polysulfide pathway.

Currently, the bioleaching of copper at large-scale production is mostly undertaken by percolation in heaps. The mineral is crushed to a particle size of approximately 1 cm or more in two to three crushing stages, cured with diluted sulfuric acid and agglomerated into small mechanically resistant spheres before stacking. An acid solution is applied on top of heaps via drip irrigation or via sprinkling and is repeated as many times as necessary to obtain the desired copper extraction and concentration. It is important to build a homogeneous heap with high void fraction in order to facilitate the percolation of the leaching solution and the upcoming gas flow injected at the bottom to provide the necessary oxygen and carbon dioxide [15–17]. The pregnant liquor then enters the recuperation section, consisting of a solvent extraction (SX) unit that purifies and concentrates the liquid in copper and copper recovery via electrowinning (EW). The leaching period may last two or more months. The heap bioleaching operation has been reviewed by several authors [15,18–21]. Figure 1 shows a block diagram of a typical heap bioleaching operation.

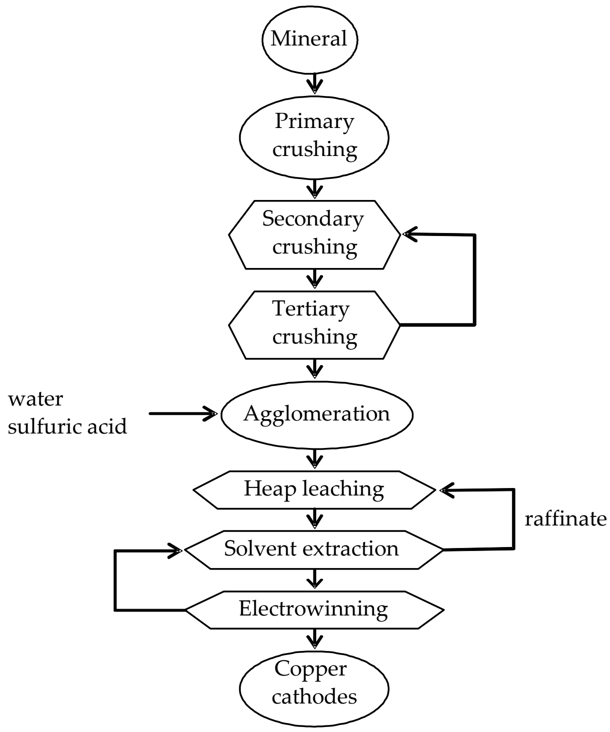

Figure 1. Block diagram of a copper heap bioleaching process [22].

2.2. Operating Factors Affecting the Bioleaching Process

No doubt the microorganisms are the main actors in bioleaching. Since heap bioleaching is not run under aseptic conditions, the native mixed population existing at the mine site takes care of the process. The inoculation of pure microbial strains or consortia has been proposed [23–25], but up to now this has not been a common practice. During heap operation, a great diversity of microbes are present, mostly bacteria and archaea [26–28]. The most well-known and first identified bioleaching bacteria are *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, and *Acidithiobacillus thiooxidans*.

In order to grow and bioleach, these microorganisms need nutrients, which they have to find in their environment [22]. Many of them become available from the same ores and leaching solution, but some of them, such as nitrogen and phosphorus, may become scarce and affect the bioleaching process [29]. These may need to be added to the leaching solution if economically feasible.

The bioleaching microorganisms need two gaseous components: carbon dioxide, as a carbon source, and oxygen, as an electron acceptor. In order to become available to microorganisms, they have to be transferred from the gas phase to the leaching solution [30]. This means that their availability will depend on the mass transfer characteristics of the bioleaching system.

Oxidation-reduction potential (ORP), pH, and temperature are important operation conditions for the microorganisms and the sulfide oxidation performed by ferric iron. In the case of pH, both phenomena are favored by low pH in the range of 1.0 to 2.0. In the case of temperature, the microbial tolerance fixes an upper limit that clearly does not benefit the ferric oxidation of sulfides [31]. In this sense, hyper-thermophile microorganisms have shown to get higher extraction percentages than mesophile ones. In the case of ORP, as bioleaching proceeds, microbial activity tends to increase the leaching solution ORP. In most cases, this is a desired condition; however, in the case of bioleaching of chalcopyrite, it has been found that intermediate values approximately 450 mV (Pt, Ag/AgCl electrode) allow extracting high percentage of copper [32].

The bioleaching rate is dependent on the type of metal sulfide. In general, the so-called primary copper minerals are much more difficult to solubilize than secondary ones. Among the former are chalcopyrite and enargite, and among the latter chalcocite, covellite and bornite.

As in any extraction process, the particle size affects the leaching rate and efficiency. The rate and extend of sulfide oxidation will depend on the specific surface area exposed to the leaching solution. In turn, high interfacial area is obtained thanks to intensive crushing of the ore. With a large particle size, the solubilization is controlled by diffusion phenomena [31].

Lastly, the bioleaching mode affects the efficacy and effectiveness of the process. Different operation modes, due to their own characteristics, condition the performance of the bioleaching phenomenon. Early attempts of bioleaching were conducted in the so-called dump bioleaching mode, characterized by a highly non-homogeneous bed of solids, constituted by rocks as big as 1 m in diameter. In this case, there is no control on the main operating variables, giving a low productivity. A much better system is the heap, where homogeneous structure improves the bioleaching conditions considerably. These are the arguments for why it is the most useful on an industrial scale. An extreme situation is the use of agitated reactors, where it is possible to exert tight control over pH, ORP, temperature, and gaseous component accessibility. However, in spite the best performance conditions that can be achieved, unfortunately, it is still too expensive to compete with heap bioleaching of copper ores [33].

3. Historical Development of Bioleaching in Chile

3.1. Early Research Efforts

In the late sixties and early seventies, the first registered studies on *Acidithiobacillus ferrooxidans*, formerly known as *Thiobacillus ferrooxidans*, were done by Manuel Rodriguez at the Faculty of Biological Sciences of the Pontificia Universidad Católica de Chile and Claudio González at the Faculty of Chemistry and Pharmacy at the Universidad de Chile. These investigations were centered mostly on the basic microbiology of this bacterium rather than in its potential application to biomining.

In the late sixties, the Chilean government established two research institutes: the Centro de Investigaciones Minero Metalúrgicas—CIMM (Mining and Metallurgical Research Center)—and the Instituto de Investigaciones Tecnológicas—INTEC (Technological Research Institute). CIMM was a joint project of the Chilean government and the United Nations Development Program (UNDP). In the early seventies, CIMM started a research project on bacterial leaching in the Potrerillos mine in the Atacama region [34].

During its start-up, INTEC received the advice of some distinguished international experts, some of them well acquainted with bioleaching technology. At that time, INTEC initiated a research project on bacterial leaching of copper ores [35].

An effort that has been ongoing up to now has been that of the School of Biochemical Engineering of the Pontificia Universidad Católica de Valparaíso that started working on the bacterial leaching of copper ores back in 1974. The first results of this line of research were presented in 1976 in the VIII Jornada Chilena de Química, Santiago de Chile. This line of research has received significant scientific and economic support from several international projects such as Metallurgical Technology-Copper from the Organization of American States (OAS), 1979–1981, Research and Development of Metallurgical Processes-Hydrometallurgy, OAS, 1982–1985, and Biotechnology Applied to Copper Mining, OAS, 1985–1988.

These research efforts have been centered in topics such as growth and oxidation kinetics of *Acidithiobacillus ferrooxidans* in defined media, inhibition effects of organics on growth and oxidation, bioleaching of model copper sulfides, bioleaching of low grade copper ores, tailings and concentrates, bioleaching of copper ores in column and stirred reactors, biooxidation of refractory gold concentrates, biooxidation in continuous single stage and multistage reactors, adaptation of leaching microorganisms to high pulp densities, bioleaching with *Sulfolobus metallicus* in flasks and reactors, and factors affecting the synthesis of extracellular polymeric substances.

3.2. The United Nations Development Program (UNDP) Project

The United Nations Industrial Development Organization (UNIDO) expert meetings in May 1982, in Lima, Peru, and Santiago, Chile aimed to explore the possibility of establishing an international center for the development of biotechnology, antibiotics, and other pharmaceuticals products in Latin America. Chilean biotechnologists convened and decided to unite their efforts to attack one important topic relevant to the country economy and development. The chosen issue was the Chilean copper mining and the contribution that biotechnology could make in that field. They felt that, due to the complexity of the problem, the project should be addressed in a multi-disciplinary and multi-institutional fashion and should include researchers from the universities, research institutes, and the mining sector, as shown in Tables 4 and 5. The project received financial support from the Chilean government and The United Nations Development Program (UNDP), and consisted in two stages, namely "Development of Biological Processes and their Industrial Application to the Bacterial Leaching of Chilean Minerals—Phase I", UNDP/CHI/85/002, 1985–1988 and "Development of Biological Processes and their Industrial Application to the Bacterial Leaching of Chilean Minerals—Phase II", UNDP/CHI/88/003, 1988–1990.

Table 4. Participants in the United Nations Development Program (UNDP) Project on bacterial leaching of Chilean copper.

Participants
University of Chile
Pontifical Catholic University of Chile
Pontifical Catholic University of Valparaíso
Instituto de Investigaciones Tecnológicas (INTEC)
Centro de Investigaciones Minero Metalúrgicas (CIMM)
Corporación Nacional del Cobre (CODELCO), Chuquicamata Division
CODELCO, El Teniente Division

Table 5. Areas and activities covered in the United Nations Development Program (UNDP) Project on bacterial leaching of Chilean copper.

Areas and activities
Molecular biology and Genetics
Microbiology
Chemistry and Electrochemistry
Chemical Engineering
Biochemical Engineering
Metallurgical and Mining Engineering
Analytical and Experimental Methodologies
Personnel Training

The project was very successful and contributed significantly to the bioleaching knowledge in those days. As a result of this experience, Chile was recognized by the United Nations Industrial Development Organization as a world leader in bacterial leaching research [36]. Several of its personnel moved to mining companies, especially to the Sociedad Minera Pudahuel (SMP), where they contributed effectively with the knowledge and experience gained in the project.

3.3. The Sociedad Minera Pudahuel (SMP) Project: Commercial Bioleaching Operation

In 1980, the Sociedad Minera Pudahuel built and commissioned the Lo Aguirre copper mine located near Santiago, Chile. This small mine obtained copper from mostly oxide minerals through acid leaching in vats. Its first important achievement was the development of the thin layer (TL) leaching technology consistent of pads three to eight meters height of agglomerated ore, which operated successfully, rendering copper at low cost.

As the oxides approached exhaustion SMP personnel realized that after some weeks soluble copper began to leak from the treated oxides. SMP established a research and development department that came to the conclusion that sulfur was oxidized by the bacterial action. This led to the design and commissioning of a successful heap leaching operation that together with a SX/EW plant produced 14,000 tonnes/year of fine copper until the exhaustion of the deposit in 2002 [15,17,37,38]. It is important to point out that the Aguirre mine was the first copper mine of the world exploited exclusively by bioleaching technology [17,39].

3.4. Large Scale Operations in Chile

During the 1990s and onward, several large-scale bioleaching operations besides Lo Aguirre were installed in different mines in Chile. The Lince-Michilla mine started its heap leaching operation in 1991 with a total production of 22,000 tonnes/year. Two important mines operating completely via bioleaching technology were commissioned in 1994, Quebrada Blanca and Cerro Colorado, while CODELCO's El Teniente Division exploited the El Crater deposit via in-place biotechnology. Other early copper heap and dump bioleaching operations in Chile were Andacollo, Ivan-Zar, and Los Bronces [40–42].

Several other bioleaching operations are near start-up or in a planning stage. Such is the case of Carmen de Andacollo, Collahuasi, Dos Amigos, Punta Colorada and Spence. Special mention should be made to La Escondida mine, currently the largest world copper mine [17,43].

4. Conclusions

In Chile the joint efforts of scientists and technologists both from the academia and the mining industry have enabled the development of a robust and growing copper bioleaching industry. Up to date an important number of commercial installations are successfully operating. It is expected that in a near future these operations will extend from the exploitation of secondary minerals to primary minerals of which Chile has vast reserves.

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