WASTE MANAGEMENT AND METAL RECOVERY IN THE CHILEAN COPPER INDUSTRY

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ABSTRACT

Chilean copper is produced by two processes: concentrators on the basis of physical separation technology, including mining, crushing, milling and flotation, obtaining concentrates (typically 28-35% Cu), and hydrometallurgical plants, including mining, crushing, heap leaching, solvent extraction and electro winning, obtaining copper cathodes (99.99% Cu). A portion of the concentrates is treated in smelters and electro-refineries, obtaining copper cathodes (99.99% Cu), while another portion is exported to be treated in international facilities.

Typical wastes generated during these local processes are acid drainage, flotation tailings, copper slag, smelter flue dusts, acid effluents, etc.

In the last few decades, the local copper industry has implemented several technologies and carried out research to manage these wastes and recover metals that contain; mainly copper, molybdenum, and iron, among others.

This paper reviews the present situation regarding waste management in the Chilean copper industry in terms of generation and characterization, as well as the operations and research carried out to recover metals from these wastes. Some suggestions are made regarding waste management and metal recovery guidelines and regulations to increase the chain value in the mining and metallurgical copper recovery process.

INTRODUCTION

Mineral deposits, along with a long mining tradition and a stable legal framework for investment, have stimulated the financing of projects and consolidated the economical development of the Chilean mining industry. These investments increased Chile's copper output, positioning Chile as the world's largest copper producer, as shown in Table 1 [1].

Table 1. Chilean copper production to exports

Final product	Production (metric ton)		World share (%)
	1990	2012	2012 (ranking)
Mine (total)	1,588,400	5,434,900	31.8 (1)
Concentrate	259,900	2,062,800	18.9 (1)
Cathode SX-EW	122,100	2,029,000	57.6 (1)
Cathode E-R	955,600	873,300	5.2 (3)
Blister and other (*)	250,800	469,200	N.A.

(*) blister and fire refined; N.A.: not available

The main copper producer is the state-owned mining company *Corporación Nacional de Cobre* (CODELCO-Chile) composed of 6 operations: Chuquicamata, Radomiro Tomic, Gabriela Mistral, Salvador, Andina and El Teniente, which produced 1.7 million tonnes of fine copper in 2012. However, the private mine Escondida is the biggest single copper producer (1.1 Mt/y), while other important operations are Los Pelambres (418 kt/y), Minera Sur Andes (417 kt/y), Collahuasi (282 kt/y), Esperanza (173 kt/y), Spence (167 kt/y), El Abra (154 kt/y), and Candelaria (123 kt/y), among others [1].

Furthermore, Chile is a globally important producer and exporter of molybdenum, a by-product obtained from copper processing, as well as of gold, silver, industrial minerals like sodium and potassium nitrate, iodine, lithium, and borates [1].

In terms of copper reserves, Chile accounts for 24% of the world total, which reached 680 Mton in 2012. Additionally, the country ranked number one in terms of worldwide exploration expenditure for copper, with 15% (690 Million US$) for the same year [2].

The Chilean Copper Commission (COCHILCO) forecast over US$ 103 billion in mining investments for the 2013 – 2010 period, where over 70% is related to copper initiatives. This should increase copper production to over 8 Mton by 2020 [2].

Generally, Chilean copper is produced by two ways:

- Concentrators, based on physical upgrading technology, including mining extraction, crushing, milling, and flotation, obtaining concentrates (typically 28-35% Cu). A portion of these concentrates is treated in smelters and electro-refineries, obtaining copper cathodes (99.99% Cu), while another portion is exported to be treated in international facilities.

- Hydrometallurgical plants, including mining extraction, crushing, heap leaching, solvent extraction and electro winning, obtaining copper cathodes (99.99% Cu).

Several wastes are generated during these processes, which must be managed and disposed of in order to meet the standards and regulations passed by the Chilean government. Additionally, local industry has implemented several technologies and carried out research to treat these wastes and to recover the metals they contain, as well as to dispose of dangerous impurities safely and thus to achieve waste minimization.

In this context, this paper reviews the present situation regarding waste management in the Chilean copper industry in terms of generation and characterization, as well as summarizing operations and research carried out to recover metals from these wastes.

ENVIRONMENTAL REGULATIONS

Since 1991, several environmental regulations have been established by the Chilean government in order to reduce emissions to the atmosphere, water (river, sea and lakes) and to the soil, as well as to manage wastes generated. Table 2 summarizes these regulations and others affecting mining operations - mainly copper smelters [3].

Table 2. Environmental regulations affecting copper smelters

Regulation (year)	Matter
D.S. 185 (1991), Ministry of Mining	Primary and secondary air quality standards for sulfur dioxide and particulate matter for all copper smelters
Environmental Law 19,300 (1994)	Environmental Impact Assessment and approval of any project affecting the environment and health of the population
Decontamination plans to reduce SO_2, PM and As emissions	Emission reduction plans for Ventanas (1992), Chuquicamata (1993), Paipote (1995), Potrerillos (1998), Caletones (1998) smelters. Setup of gas handling system, including sulfuric acid production and handling of flue dusts and acid effluents.
D.S. 165 (1999), SEGPRES	Arsenic emission standard for all copper smelters
D.S. 90 (2000) CONAMA	Discharges of industrial wastes into water. For example in fresh water: sulfate (1,000 mg/L), Mo (1 mg/L), As (0,5 mg/L)
D.S. 184 (2003) Sanitary Regulation on Handling of Dangerous Wastes	Controls all operations producing over 12 t/y of dangerous wastes or 12 kg/y of very toxic wastes, which must be identified and classified, and standards about its storage, transport, reuse and recycling, incineration and final disposition are applied (*)
Law 20,551(2012)	Mine closure regulation, including technical, safety and financial issues for large, medium and small scale operations
New As emission standard (2013)	Update D.S. 165 with a new As emission standard applied to copper smelters and other sources of As emissions. Also, this standard will allow the reduction of SO_2, PM and Hg emissions.

Note: (*) Massive mining wastes, including waste rock, low grade ores, leached residues, flotation tailings, and slag are excluded. However, EPA TCLP test may be requested in order to determine the hazard involved.
Note: SO_2: sulfur dioxide; PM: Particulate Matter; As: Arsenic; Hg: Mercury; Mo: Molybdenum

Copper smelters

Between 1992 and 2002, copper smelters invested over US$ 1.5 billion (US$ 1,526 per ton S recovered) in their operations to conform with the air quality standard (SO_2 and PM) and arsenic emissions standard, while smelter production increased from 1.2 to 1.4 Mt/y. This means that global SO_2 capture increased from 20% to over 80%, and PM emissions were reduced from over 9 to 3 kt/y in the same period [4].

In order to fulfill the new SO_2 and As emission standard in the next 5 years, these smelters have to invest other US$ 1.5 billion, as SO_2 and As capture are expected to be increased to 95%. Table 3 shows SO_2 and As emissions from copper smelters, as well as the present and new emission standard to be reached by 2018 [5][6].

Table 3. SO_2 and As emissions from copper smelters and the present and new emission standard to be reached by 2018

	Sulphur dioxide emissions (t/y)			Arsenic emissions (t/y)		
Smelter	Present standard	Average 2007- 2011	New standard by 2018	Present standard	Data 2011	New standard by 2018
Chuquicamata	56,600	92,104	49,700	800	520	476
Caletones	230,000	118,642	47,680	360	250	130
Potrerillos	100,000	82,258	24,400	800	600	157
Altonorte	24,000	44,251	24,000	126	97	126
Ventanas	90,000	18,820	14,650	120	90	48
Chagres	14,400	13,437	13,950	90	3	35
Hernán Videla Lira	40,000	23,021	12,880	34	12	17
Ministro Hales (*)	-	-	548	-	-	1

Note (*): roasting plant starting operation by 2014.

WASTE MANAGEMENT AND METALS RECOVERY

Concentrator plants

Copper production in concentrate form was 3.4 Mt Cu in 2012, of which 60% was exported. This production was mainly obtained from 12 large-sized operations (> 50 kt/y Cu output) and 10 medium sized operations (between < 50 and > 2 kt/y Cu output).

A typical flowsheet for the treatment of sulfide ore to obtain copper concentrates in Chile by large and some medium scale copper mining operations is shown in Figure 1, indicating the main liquid and solid wastes generated [7].

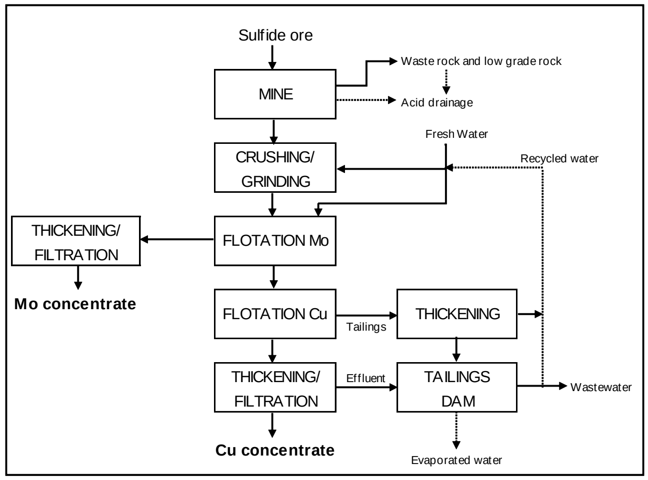

Figure 1. Flowsheet for copper sulfides

Acid drainage treatment

Normally, copper mines associated with concentrator plants are located in the northern part of Chile, in the Atacama Desert, one of the driest places in the world. This condition, together with the alkaline soils, allows the avoidance of the generation of acid drainage.

However, in the central zone of the country, with a normal high precipitation rate but with snow, where El Teniente mine is located, acid drainage has been generated by natural leaching of the low grade mineral remaining in old underground exploration and exploitation zones.

This solution is collected using several pipe lines and transported to a hydrometallurgical plant (started in 1984 with an investment of US$ 17 million) as shown in Figure 2. Copper production capacity is 6 kt/y, while annual average production in the last 10 years was 4kt, mainly due to a drop-off in copper concentration in the drainage [7].

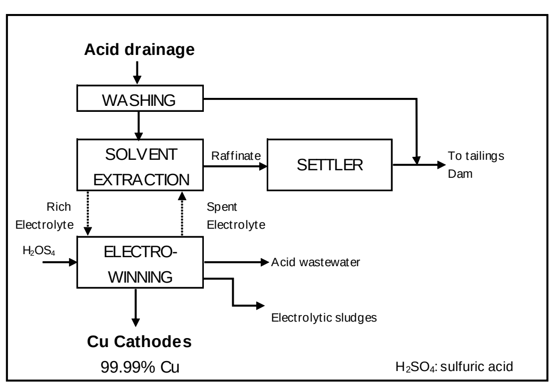

Figure 2. El Teniente hydrometallurgical plant to treat acid drainage

Another plant was built in 1999 at Minera Sur Andes to treat the solution obtained by natural and acid leaching of the low grade mineral from the San Francisco deposit. This solution was further treated by SX-EW to obtain copper cathodes. Annual capacity production was 15 to 24 kt of copper, depending on the flowrate to be treated. Note that during the driest periods (without rain or snow) the raffinate solution was completely recycled to the leaching circuit, while during rainy periods, it was sent to a neutralization plant (380 l/s capacity) using lime [8].

Tailings

It is estimated that a mine producing 500 kt/y of copper in concentrate would generate around 50 Mt of tailings [9]. In this context, according to the copper concentrate production of 3.4 Mt in 2012, the generation of tailings should be over 300 Mt from over 20 large and medium size concentrator plants operating in the country.

This massive mining waste is finally disposed of in tailings dams as pulp, where water is normally recycled to the concentrator, though disposal in paste form is being adopted by several operations in order to reduce water consumption.

Regarding metal recovery from these tailings, research has been carried out to recover the iron contained, mainly in the Atacama region of the northern part of Chile.

Since 2008, the Magnetite plant operated by Compañía Minera del Pacífico (CMP) treats old and fresh tailings from a concentration plant operated by Minera Candelaria, a subsidiary of Freeport-McMoRan Copper & Gold. The investment was about US$ 70 million to produce about 3.5 Mt/y of iron ore concentrate (> 68% Fe), which is exported [10].

The processing plant includes magnetic concentration (Rougher), milling, magnetic concentration and flotation (Inverse pneumatic). A typical chemical analysis of tailings generated from the copper flotation process is shown in Table 4.

Table 4. Chemical analysis of copper tailings (%)

% solid	Fe T	Fe Mag	P	S	SiO_2	CaO	MgO	Al_2O_3
30	18 – 22	10 -13	0.2 – 0.4	1 - 4	40	3.5 – 4.0	3.5	8 - 9

Some technical challenges in this type of operation are related to the variability of the iron content and the high sulfur content in copper tailings, which could affect the quality of the iron ore product.

On the other hand, since 2011, EcoMetales Limited is operating the Planta de Tratamiento de Residuos Mineros (PTRM) of Chuquicamata, which treats the fresh tailings in order to recover the fine fraction of the copper contained, as well as molybdenum. The process includes cascade, rougher and column flotation, while sulfuric acid is added in the feed. Additionally, the company is studying the alternative to treat the coarse fraction of tailings, as well as the old tailings, which could have up to 0.4% of copper content [9].

Since 1992, the private company Valle Central, an Amerigo Resources's subsidiary, has a contract with Codelco's El Teniente Division to process its fresh tailings, as well as the old tailings deposited at the Los Colihues tailings dam [11][12]. Its processing capacity is 175 kt/d (130 kt/d as fresh tailings) in order to recover 20 kt/y of Cu and 350 t/y of Mo in concentrate form, from:

- Fresh tailings and coarse old tailings, where the fine fraction from hydrocycloning feeds the cascade flotation, obtaining a pre-concentrate (0.35% Cu, 4.2 kt/d), which is sent to a rougher flotation step, while the coarse fraction is processed by ball milling and rougher flotation, followed by re-milling and column flotation to obtain a Cu-Mo concentrate.
- Fine old tailings (22 kt/d) are leached by sulfuric acid (9-12 kg/t tailing), followed by precipitation using NaHS (0.9 kg/kg soluble Cu) to recover Cu from oxides as a CuS concentrate (60% Cu).

Smelting and electro refining

Smelter production in 2012 was 1.4 Mt Cu from 7 facilities: Codelco (Chuquicamata, Potrerillos, Ventanas and Caletones), Altonorte (Glemcore-Xstrata), Hernán Videla Lira (ENAMI) and Chagres (Anglo American), while refining production was 873 kt from 3 facilities operated by Codelco (Chuquicamata, Potrerillos and Ventanas) [1].

Smelting furnaces used in these facilities are based on Flash, Teniente converter or Noranda technology with blister copper production capacities varying between 100 to 580 kt/y. Figure 3 shows the main and auxiliary technologies during smelting and refining processes, while Table 5 shows an estimated generation of the main liquid and solid wastes [9].

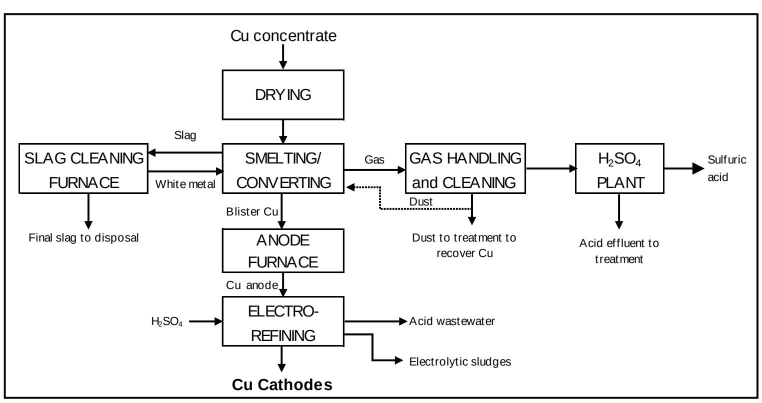

Figure 3. Typical smelting and refining process in Chile

Table 5. Estimated generation in Chile for wastes from smelting and refining

Waste	Unit	Quantity
Smelter slag (7 facilities)	Ton/year	3,000,000
Smelter flue dust (7 facilities)	Ton/year	110,000
Acid effluent (acid plants)	m^3/day	4,100
Acid waste water (3 refiners)	m^3/day	1,200

Copper recovery from smelter flue dusts

Typical gas handling and cleaning systems used by copper smelters include settling chambers, scrubbers and electrostatic precipitators to clean gases and recover dusts. The cleaned gases, containing SO_2, are treated in plants to produce sulfuric acid, which is used in hydrometallurgical processes.

Dust contains typically Copper (3 - 30%), Arsenic (1 - 17%), Sulfur (0.8 - 13%), Bismuth (0.1 - 0.9%), Lead (0.2 - 20%), Iron (0.5 – 12%), Antimony (0.1 – 1.5%), and other elements [9].

In 1982, Codelco's El Teniente Division built a hydrometallurgical plant to treat flue dusts from the Caletones smelter, which is still in operation. The original process included acid leaching of dusts, Bi recovery, and As precipitation as amorphous ferric arsenate, while copper contained in the leached solids is sent back to the smelter and that reporting to solution sent to the SX-EW plant used to treat acid drainage, which was described previously. Figure 4 shows a flowsheet of this original process [13].

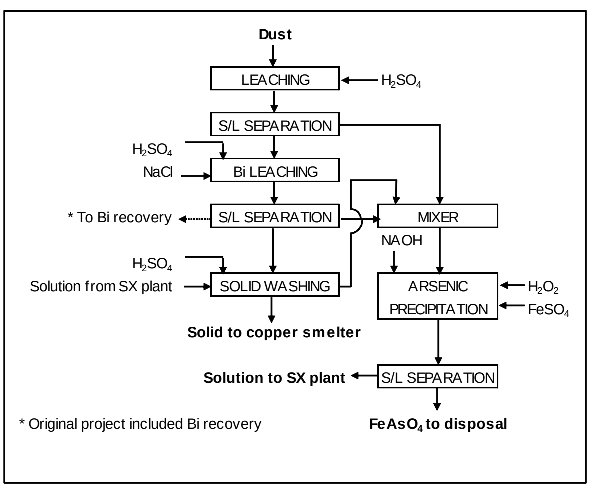

Figure 4. El Teniente hydrometallurgical plant for treating copper flue dust

Some technical challenges in this operation have been a lack of stability of the Cu and As concentration in flue dusts, affecting process performance; Bi recovery not being carried out due to market conditions, and the final residue not reaching the EPA TCLP test for Cd according to D.S. 148 regarding the handling of dangerous wastes [13].

Since 2007, EcoMetales Limited, a Codelco subsidiary, has treated over 300 kt of flue dusts and other wastes and recovered over 54 kton of copper at its plant located in the Chuquicamata facilities. Today this plant has the environmental approval to treat 75 kt/y of dangerous waste, mainly flue dusts and refinery effluents (about 1,000 m^3/day), corresponding to an abatement capacity of 10 kt/y of As and Sb [9].

Flue dusts from Chuquicamata, Potrerillos and Ventanas smelters are leached with sulfuric acid, after which leached slurry is sent back to the smelter, while Pregnant Leach Solution (PLS) is treated with a ferric solution to precipitate As at atmospheric pressure as Scodorite (crystalline ferric arsenate) together with other impurities like Sb, as shown in Figure 5. Cleaned solution is then sent to the SX-EW facilities at Chuquicamata, while final stabilized residue is sent to disposal in order to meet regulation D.S. 148.

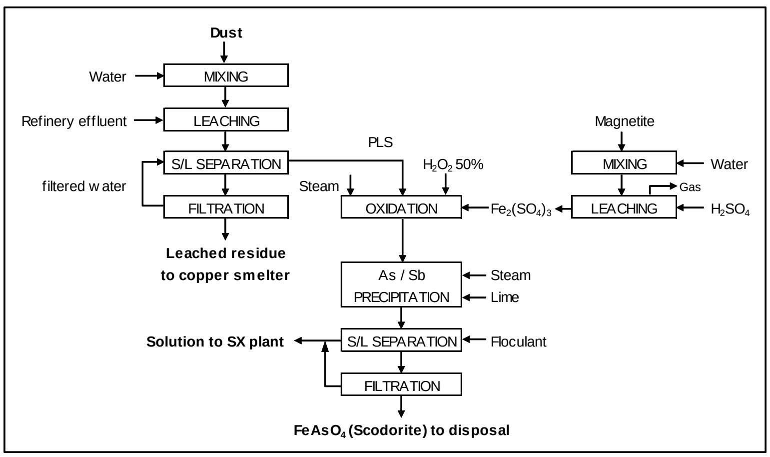

Figure 5. Ecometales hydrometallurgical plant for the treatment of copper flue dust and precipitation of As and Sb [14].

A new focus of research for EcoMetales Limited is the recovery of other metals contained, either in the PLS solution or the leached residue, such as Mo, Re, Ge, Pb, Ag, etc. In the case of Mo, a study was carried out to recover it by ionic exchange from the solution (0.3 g/L Mo) in the form of a molybdate of ammonium [9].

Slag

Copper slag is a crystallized mixture of metal oxides and silicates generated in copper smelting and converting, which are normally disposed of. A slag contains typically Copper (0.8 – 1%), Molybdenum (0.2 – 0.3%), Iron (30 – 45%), Silica (35 – 40%), and Alumina + Calcium Oxide (< 10%).

Annually, over 3 Mt are generated from all the copper smelters operating in Chile and it is estimated that between 40 and 50 Mt are already deposited near these facilities, which represent an interesting business potential to recover the metals contained.

In this context, extensive lab research has been carried out to determine their physical and chemical characterization, as well as ways to recover Cu, Mo, Fe, and other elements. Hydro and pyrometallurgical routes have been proposed, including a milling, roasting-leaching, IX and SX-EW flowsheet, as shown in Figure 6.

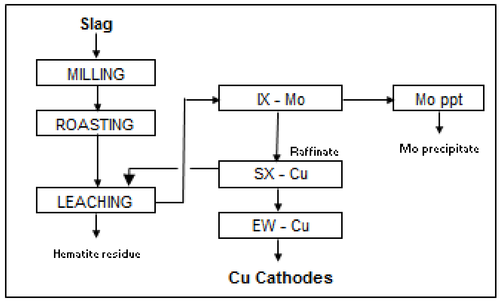

Figure 6. Proposed hydrometallurgical route to treat slag and recover metals [15].

Regarding this proposal, no pilot plant has been carried out yet, and more research is required to solve some challenges, such as proper separation of Mo-Fe and high acid consumption [15].

Additionally, alternative uses of slag could be allowed, for example, as building materials or for road construction, as practiced in international markets such as Europe, India or China.

<u>Liquid Effluents from acid plant</u>

Sulfuric acid plants generate arsenic-containing effluents, which are treated in effluent treatment plants. Normally, the solution is neutralized and arsenic is precipitated as calcium arsenite, $CaAsO_2OH$, and calcium arsenate, $Ca_2AsO_4(OH)$. In addition, calcination is used to produce a stable product, $Ca_3(AsO_4)_2$ [16]. However, this process normally generates a treated effluent with a high content of As (about 150 ppm), as well as, a large quantity of arsenical residues to be disposed of.

In this context, EcoMetales Limited is working on a new process to be used at the acid plant in Codelco's El Teniente Division, where today arsenic bearing acid effluent is being treated with lime, obtaining a treated effluent with a residual As concentration and a significant quantity of solid arsenical waste. The new proposal includes As precipitation as As_2S_3 using sulphidric acid generated *in situ* in bioreactors. This plant should process around 700 m^3/d of effluent to obtain a treated effluent with a very low level of residual As, while the quantity of solid arsenical residue should be reduced in quantity by 4 times, as compared to lime treatment.

Refinery sludges (anodic slimes)

Over 1 kt/y of anodic slimes are generated from three Codelco refineries, of which a small portion is treated at the Ventanas facility, while the rest is exported, mainly to Europe and Japan [9]. Normally, this product contains copper (25%), precious metals (0.17% Au and 17% Ag), PGM`s (Pd, Pt), Te, Se, and others, which have strategic applications in several industries.

At present, Codelco has submitted plans for Environmental Evaluation to the Ministry of the Environment in order to build a 4 kt/y processing capacity plant at the Mejillones complex in the Antofagasta Region, using the technology proposed by the South Korean company LS Nikko Copper Inc. The investment is estimated to be in the range of US$ 80 million and construction is expected to start by 2014. Expected annual metal production, depending on the metal content in the anodic slimes, is 5 t Au, 500 t Ag, 150 kg Pd, 10 kg Pt, 200 t Se, 20 t Te and 1.6 kt of copper sulfate [17].

Leaching, Solvent Extraction and Electro Winning

Over 2 Mt of copper are produced in Chile from oxide and secondary sulfide ores using leaching, Solvent Extraction (SX) and Electro Winning (EW) processes. There are over 30 operations, of which 13 are large-sized (> 50 kt/y Cu production). A typical flowsheet is shown in Figure 7 [7].

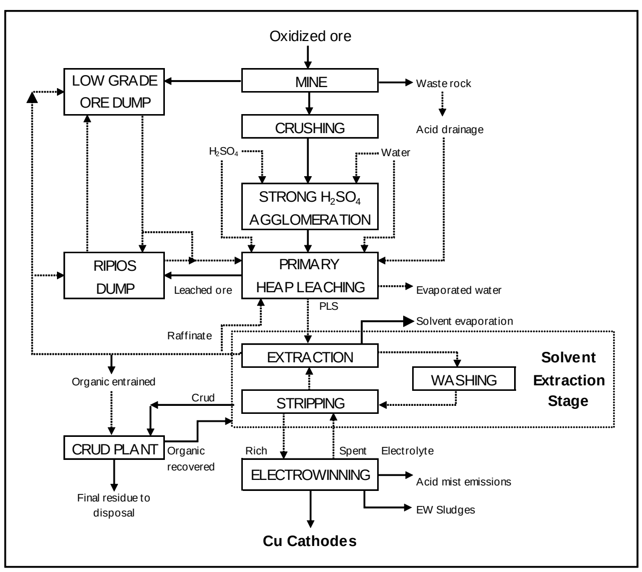

Figure 7. Flowsheet of copper oxidized ores

Copper recovery from solution has been the main focus in these plants, but recovery of Mo as trioxide from SX solution (2 g/L Cu, 0.3 g/L Mo and pH 2) has been studied. The main topics to be resolved are the Mo removal from the Cu SX organic phase, a complex Mo aqueous phase chemistry, very low Mo stripping reaction kinetics compared to the extraction reaction, and a better understanding of the right residence time and mixing, which are critical factors for the efficiency of the Mo removal process [18].

CONCLUSIONS

Chile is the world`s largest mining copper producer with an important investment and projects pipeline for the next decade, in which waste management and metal recovery is crucial to achieve the sustainable development of the mining and metallurgical industry.

Copper recovery from acid drainage, tailings and flue dusts, as well as iron from copper flotation tailings are good examples of this. However, additional technological research and development, as well as cooperation are needed to recover other metals contained in mining wastes.

In this context, EcoMetales Limited is working in different fields to improve mining waste management and treatment, including metals recovery like Mo, to become a world leader in environmental solutions for mining waste, making its treatment economically viable through the recovery of metals.

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