Management of copper pyrometallurgical slags: giving additional value to copper mining industry

*Universidad de Concepción, Chile
†Universidad de Atacama, Chile

In past years, Chile has been the largest copper producer in the world and for 2002 mining represented 10% of the GDP, accounting for 47% of the total exportation. As copper sulphides are the main mining resources in the country, the metal is produced using the classical processes of flotation and pyrometallurgical extraction. Seven copper smelter plants, which extends from the northern Atacama desert to the central part of the country produced 1,522,000 metric tons of fine copper in 2002, approximately one half of total copper concentrate production, with a notorious environmental impact due to the great amount of slag produced during these extraction steps.

In this work, a global characterization of copper pyrometallurgical slags produced and disposed of in Chile and worldwide is done, and the concept of total project development is considered to explain the scopes of the study, recovering different compounds and generating new activities around mining.

The presentation is completed with the proposal of various methods and techniques being developed today in a joint project between smelter plants and the University of Concepción, with the support of the Chilean government and mining companies, addressed to generate new materials from copper slag. Recovery of copper, molybdenum, precious metals, silica and iron, that is the most abundant component of the slag, are the goals for this research. Metals, commercial compounds, alloys and different forms of iron oxides for steel industry are proposed products.
Some previous studies have been considered\textsuperscript{4-5}. Among other interesting papers are notable patents reporting flow sheets for specific processes to treat copper slag. In this case, the proposal is to establish methods and techniques for treating slag produced in Chilean smelter plants as the first approach.

Given the high concentration of smelter plants in Chile\textsuperscript{6}, the intensive production of slag causes major trouble in transport and disposal. Then, use of this waste gives additional value to the mining-metallurgical business which is much appreciated. Therefore, this project has the support of Chilean government by the National Commission of Scientific and Technological Research, CONICYT\textsuperscript{7}.

Characterization of slag: the chilean case

Some properties of a typical copper slag are shown in Table I, and it can be observed that air-cooled copper slag has a black colour and glassy appearance. The specific gravity varies with iron content, from 2.8 to 3.8. The unit weight of copper slag is somewhat higher than that of conventional aggregate. The absorption capacity of the material is typically very low. Granulated copper slag is more porous and, therefore, has lower specific gravity and higher absorption capacity than air-cooled copper slag. The granulated copper slag is made up of regularly shaped angular particles, mostly between 4.75 and 0.075 mm\textsuperscript{3}.

Slags produced during pyrometallurgical processes have been traditionally considered as a waste\textsuperscript{3}. In the case of copper extraction processes, it has been estimated that for every ton/year of copper produced, 2.2 ton/year of slag is generated, and approximately 24.6 million ton/year of slag is generated in the world copper production. In Chile, blister copper production is approximately 1.5 million tons, and more than 3.5 million tons of slag are produced every year\textsuperscript{6}. Additionally, around 50 million tons of slag have been estimated to be historically stocked in this country.

Typical analyses of various copper slags reported by Gorai\textsuperscript{8} are shown in Table II. In this table, slags from different origins are presented, named: (1) Iranian National Copper Industries; (2) Etilbank Ergani Copper Plant, Elazig, Turkey; (3) Caletones Smelter Plant, Chile; (4,5,6,7) Various Indian Copper Plants; (8) Kure Copper Slag and (9,10) Copper Queen , Prince, USA.

Recently, data corresponding to the seven smelters plants operating today in Chile have been reported\textsuperscript{6}, and they are summarized in Table III. In this table slag corresponding to flash smelting furnace, Teniente converter, Peirce-Smith converter, Anode and fire refining furnaces, and reverberatory furnaces are described.

The average composition of final copper slag corresponds to 30–40 % iron, 35-40% silica, less than 10 % of alumina and calcium oxide and copper content is less than 1%, depending on the method used to clean the final slag of the pyrometallurgical process. Eventually, minor amounts of zinc, molybdenum and noble metals such as gold and silver are presented. Since, final copper slag contain around 1% of copper, its recovery from the slag could be economically accepted if no expensive treatments are found, such as techniques mixing pyro and hydrometallurgical processes or concentration by flotation as it has been established in some concentration plants.

Wastes as resources: the total project development, a new philosophy

Total Project Development (TPD) is a new holistic approach for mining, where the project is not an isolated operation, but is part of a wide and multi-activity regional development. Under this concept, every extracted material is considered for constructive usage, establishing a range of economic activities in this way. Waste rock, mine tailings, excess mine water and even industrial garbage are considered part of the resource, and as raw material for a variety of downstream ancillary industries\textsuperscript{2-3}. Even when this concept has been applied mainly to tails from concentration plants\textsuperscript{8-9}, its philosophy is valid for slag recovery, which is the objective of this research.

The concept of TPD are from initial research to recycling of mine tailings. Thus, TPD investigated the feasibility of

\begin{table}[h]
\centering
\caption{Physical and mechanical properties of a typical copper slag, from\textsuperscript{3}}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|}
\hline
Property & Black, glassy, more vesicular when granulated & & & & & & & & & \\
Unit weight & 2800–3800 (kg/m3) & & & & & & & & & \\
Absorption & 0.13 % & & & & & & & & & \\
Bulk density & 144–162 lbs per cubic foot & & & & & & & & & \\
Conductivity & 500 µs/cm & & & & & & & & & \\
Specific gravity & 2.8–3.8 & & & & & & & & & \\
Hardness & 6–7 Moh & & & & & & & & & \\
Moisture & < 5 % & & & & & & & & & \\
Water soluble chloride & < 50 ppm & & & & & & & & & \\
Abrasion loss & 24.1 % & & & & & & & & & \\
Sodium sulphate & 0.90 % & & & & & & & & & \\
soundness loss & & & & & & & & & & \\
Internal friction angle & 40–53 & & & & & & & & & \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Chemical compositions of typical slags, from\textsuperscript{3}}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline
Origin & Fe % & SiO\textsubscript{2} % & CaO % & MgO % & Al\textsubscript{2}O\textsubscript{3} % & S % & Cu % & Co mg/kg & Mn mg/kg & Ni mg/kg & Zn mg/kg \\
\hline
1 & 44.78 & 40.97 & 5.24 & 1.16 & 3.78 & 1.06 & - & - & - & - & - \\
2 & 39.65 & 31.94 & 3.95 & 2.82 & 2.4 & - & 1.01 & 1040 & 420 & 150 & 7220 \\
3 & 41.53 & 37.13 & - & - & 2.4 & - & 0.11 & 0.79 & - & - & - \\
4 & 47.8 & 29.9 & - & - & - & - & 0.7 & - & - & - & - \\
5 & 44.7/47.7 & 28.5-32 & 1.6–3.9 & - & - & 0.3–0.9 & 0.5-0.95 & Tr–8 & - & 14–20 & 1700–2850 \\
6 & 47.13 & - & - & - & - & 1.47 & 0.68 & 2200 & 300 & 500 & 500 \\
7 & 48 & 28 & - & - & - & 0.6 & 1300 & - & 44 & 600 & - \\
8 & 47.8 & 26.1 & 0.7 & 1.0 & 6.8 & 1.5 & 0.82 & 4000 & - & - & 1500 \\
9 & 44.8 (oxide) & 24.7 & 10.9 & 1.7 & 15.6 & 0.28 & 2.1 & - & 4000 (oxide) & - & - \\
10 & 34.62 (oxide) & 27.16 & 17.42 & 3.51 & 14.7 & 0.33 & 1.64 & - & 4900 (oxide) & - & - \\
\hline
\end{tabular}
\end{table}
stand-alone tailings recycling within mining operations, and it incorporated metal retrieval, decontamination and physical utilization including underground backfill, embankments and sealants, infilling of open-cut voids, and production of construction materials for mine use. The residue is amended for use as topsoil replacement in mine rehabilitation and landscaping.

Total Project Development is desirable for technical, political, social and environmental aspects, and there is no doubt that every party associated with such a TPD scheme benefits; the mining company, regional and national governments, local community, environment and ultimately, the global community.

The mining company benefits from additional revenue through the retrieval of metals and minerals. Operational expenses are reduced for maximum utilization of tailings and others kinds of wastes. Mining and rehabilitation costs are considerably reduced with the removal of solids generated during the process. The long-term risks of potential liabilities from tailings dams and waste dumps are also removed. Relationships with local communities are vastly improved with the close co-operation associated with TPD, like those with regulatory bodies and environmental agencies, with the major knock-on effect of improving the prospects of obtaining future leases, permitting and funding for subsequent projects.

Since reduced environmental impact, diversity of associated industries, alternative employment opportunities, intermediate technologies, range of products and long-term post mining land-uses associated with TPD are fundamental for sustainable regional development, the TPD approach, especially in the Third World, offers to the mining industry a future compatible with social and environmental needs, aiming for sustainable development.

In Chile, the application of TPD approach will help to solve directly a real problem in the mining and metallurgical industry today, which is the transport and disposal of the slag. There are around 50 million tons of slag already accumulated in the country, and there in sufficient areas for disposal close to smelter plants. Thus, the approximated 4 million tons of slag generated per year in Chile causes an increase in cost of transport, due to the longer distances to cover. Therefore, any additional value for this waste will enhance the interest in developing new processes.

**Recovery of byproducts**

**Chilean experience**

Some experiences on recovery of products contained in slag have been developed in Chile as well as worldwide. As a primary copper producer, the main objectives of Chilean plants have been focused on copper recovery only, explained later. In fact, all Chilean smelter plants have their own processes, in use, most of them associated to pyrometallurgical techniques. Among Chilean experiences on this subject, the following can be mentioned:

**Slag stabilization in asphalt base**

This is a project developed by Sociedad Minera Pêtreos Quilín, and the main idea is to use sand, refractory material and smelting slag for asphalt manufacture in order not to dispose of the slag near rivers and damp, avoiding the contamination by heavy metals always present in slag and the susceptibility of dissolution into underground waters. Thus, neutralization of slag by using it in an asphalt matrix has been considered a good solution.

**Slag cleaning by coal reduction**

In this process the slag produced by the Teniente Converter is transferred to a cleaning slag furnace (HLE), and pulverized coal is injected maintaining the slag temperature by means of oxygen-fuel burners. The coal reduces the content of magnetite in the bath, decreasing slag viscosity, and copper particles are released forming a rich copper matte (70% Cu) that is returned to the Peirce Smith Converter.

**Slag cleaning in an electrical furnace**

In this process copper is recovered by direct electrical reduction of magnetite, releasing the suspended inclusions allowing co-reduction of cuprous oxide. The current
technology is based on preheating and reduction of the slag in an electrical furnace AC. In this furnace oxides are reduced by the graphite electrodes and supplementary coke addition\textsuperscript{12-13}. The immersion of graphite electrode in the bath produces direct reduction of magnetite, which generates a gas film separating liquid slag from the coal. At the coal/gas interface Boudouard reaction takes place and at the gas/slag interface magnetite and cuprous oxide are reduced by the carbon monoxide. The same reaction occurs at the carbon/slag interface. The gas generated produces bubbles that ascend and react with oxides in the slag phase. Then the metallic phase is generated and treated in another furnace to obtain Blister Copper. This process is operating at Paipote and Las Ventanas Smelter Plants, both owned by ENAMI (National Mining Companies)\textsuperscript{14}.

**Slag flotation**
The basic idea is to obtain a copper concentrate by using flotation techniques. This process was used in the past still exists as a slag treatment plant in Chuquicamata. This technique was also used widely by small miners because it is a very simple and effective way to recover copper. The slag flotation has become less important recently due to the decreasing of copper content in final slags, this was caused by new optimization methods in smelting processes. In Chile, Altonorte smelting plant, owned by Noranda, still continue using the flotation process for slags treatment.

**International experiences**
In Russia, by processing slags in electrical furnaces it has been possible to recover 98% of copper and 96% of precious metals in a metallic phase. Also, a Cyanide-Free process has been developed to separate copper and zinc contained in a concentrate, improving extraction of nonferrous and precious metals\textsuperscript{15}. Additionally, other studies have been reported on treatment of wastes containing As, Sb, Pb, Bi, Cu, S, etc., by smelting in an arc electrical furnace to obtain a metallic phase for recovering precious metals and copper after further purification\textsuperscript{16}.

The Mintek Company developed a technique for recovering cobalt, nickel and copper from a wide spectrum of smelting slag. The treatment in this case works parallel to the normal smelting operation, using an arc electrical furnace\textsuperscript{17}.

In Zambia, great amounts of slag from reverberatory furnaces has been dumped containing 1–3% of cobalt and 1.5% of copper. Currently, this slag is being processed in a copper-nickel melting plant located in Kola using an electrical furnace. The slag is melted to obtain metallic phase containing cobalt and copper\textsuperscript{18}.

The Ausmelt Company has commercialized several applications of the Ausmelt top-submerged lancing process. Cleaning of copper-nickel-cobalt slag has been implemented commercially by Rio Tinto, Zimbabwe and Anglo American Corporation. In each plant, a single Ausmelt furnace using a multitube process is applied\textsuperscript{23}.

In U.S., an important number of patents related to processes and techniques addressed to recover metals and/or other materials from slag were developed before 1978. In this year a process for reducing molten slag by carbon injection was patented\textsuperscript{8}. This process enables the recovery of metals from iron-copper slag of copper smelting furnaces, and iron-nickel slag produced in the smelting of nickel-bearing ores. In this process, the molten slag is fed to an electric-arc furnace wherein a molten metal bath is formed. The difference with other processes is given by a carbon injection unit, including an injector tube, which is inserted into the furnace.

Some processes using Hydrometallurgical techniques have also been developed. At the Universidad de Sevilla, Spain, a bioleaching process named Brisa has been addressed to treat non-iron metallic sulphides and refractory minerals containing gold and silver. It is a non-expensive bacterial process for pretreatment of auriferous pyrites, followed by cyanidation to recover precious metals. Further, liquor is treated by solvent extraction (SX) and electrowinning (EW), to obtain pure metal. Two objectives have been considered as priorities in this case: to recover metal (Cu) and also to obtain a by-product (fayalite) usable for other industrial applications, such as construction\textsuperscript{19}.

Additionally, studies on the recovery of copper, cobalt, nickel and zinc contained in slag using hydrometallurgical treatment, were reported in Holland. This process includes a roasting pretreatment and a subsequent leaching with sulphuric acid\textsuperscript{20}.

Due to American environmental regulations, important efforts have been made on dissolution of metals contained in wastes prior to its disposal. Thus, studies on recovering nonferrous metals from smelting slag and dusts by means of solvent extraction have been conducted\textsuperscript{21}.

In Turkey, a process for treatment of ancient copper smelting slag has been proposed. In this process, copper and cobalt are recovered in metallic form and/or as compounds, whereas iron is recovered as magnetic oxide or pigment, and abrasive material is produced using final reduced slag. The process stages include carbothermal reduction in a DC arc furnace, granulation, leaching, chemical precipitation, selective sulphidizing roasting and product preparations. The results of this work show that the influence of granulation on leaching process is very important\textsuperscript{24}. The copper concentration in Kure copper slag was 0.82%.

In Japan, researchers aim to reuse some wastes such as municipal ones, slag and sludge, in order to recover nonferrous metals such as cobalt and copper, have been also conducted\textsuperscript{22}.

**Expected results and discussion**
The project presented to the Chilean National Scientific and Technological Commission, includes three kinds of studies: Gravimetric and/or magnetic concentration, Hydrometallurgical and Pyrometallurgical treatment. In order to carry out these experiments, previous steps of comminution and classification is considered. This approach is presented in the flowsheet shown in Figure 1.

**Gravimetric and/or magnetic concentration**
Since, essentially, iron oxides and silica compose the slag, a good response to gravimetric and magnetic treatment is expected. As first approach, if comminution has been optimal, a separation between higher and lower density compounds producing two concentrates is considered. That means precious metals, copper and part of iron oxides in one side, the rest of iron oxides, silica and others light compounds on the other.

The influence of particle size on liberation of components is studied, and an important aspect of this research is the energy consumption during comminution. Thus, in order to minimize this parameter, the influence of granulation in
Several kinds of unit processes for gravimetric separation are used. Finally, heavy and light fractions of solids are obtained. The light fraction containing most part of silica could be recycling to the copper smelting as flux, and the heavy fraction is treated in a magnetic concentrator obtaining two fractions: magnetic iron oxide for iron pellet production and non magnetic fraction for leaching process, as shown in Figure 1. The objective of this part of the research is to obtain three well-defined byproducts in order to make more efficient progress.

**Hydrometallurgical treatment**

Hydrometallurgical routes depend on the kinds of compounds wanted to obtain. Thus, cuprous sulphide, cuprous oxide and metallic copper are the most likely components to be obtained in the case of copper. These compounds require oxidant conditions and usually high temperature in order to get copper in solution. Therefore, leaching tests are programmed using different oxidant and leaching agents in agitated system. Given the technical feasibility, the chance of success of one of these alternatives depends on issues such as the amount of copper and metals contents in the slag.

Another alternative for simplifying the treatment is to modify the compounds through an oxidative roasting step obtaining an oxidized calcine. In this case, the copper compounds could be transformed to cupric oxide or cupric sulphate, that are easily dissolved in diluted acid solution at room temperature. However, formation of cupric ferrite must be avoided during roasting.

For slag containing important quantities of molybdenum with appreciable solubility in sulphuric acid solution, it can be leached with cupric oxide in the same stage. After leaching, solvent extraction and ion exchange to separate the dissolved metals, is evaluated.

The iron compounds obtained are hematite and magnetite, which are insoluble during leaching the step and they pass to the solid residue. This residue can be concentrated for iron recovery or can be considered for other commercial use. The diagram for these two approaches is shown in Figure 2.

Precious metals contained in slag are usually in concentrations of 5 or less ppm for silver and less than one ppm for gold, which requires being concentrated prior to the hydrometallurgical treatment.

**Pyrometallurgical treatment**

For Pyrometallurgical treatment, three possibilities have been considered: roasting of slag, high temperature oxidation of fayalite and direct reduction of iron oxides. Roasting has been considered in order to obtain a product able to be leached to dissolve copper and precious metals. Based on thermodynamics considerations for the equilibrium of different compounds present in slag, the possibility of obtaining soluble copper compounds and
insoluble iron oxide is well known as presented in the Kellogg diagram shown in Figure 3, at 600ºC. As could be expected at this temperature, copper sulfate and hematite could be formed. Then, avoiding formation of copper oxide, copper ferrite would be minimized.

For fayalite oxidation, additional to high temperatures, oxygen potential of about $10^{-6}$ atm is required to ensure the reaction

$$3(2FeO \cdot SiO_2) + O_2 = 2Fe_2O_3 + 3SiO_2$$

Since, at high temperatures both magnetite and silica melt, it is not certain these products would be solid or at least very viscous during the process. Additionally, risk of copper ferrite formation exists if some copper oxide is present while magnetite is formed.

The third consideration is direct reduction of slag to reduce iron oxides to metallic iron, and then to obtain iron-copper alloy. In fact, this possibility exists today in copper smelter plants during slag cleaning processes which, actually, is addressed to reduce magnetite to less oxidized states of iron. The limitation of this process in the smelter plant is given by the final metallic phase to be obtained, which must be recycled to the process, and this phase must be clean of iron not to contaminate copper production. However, reduction could be forced to iron production if it is done in a separate vessel, after the copper production is completed.

In Figure 3, Chaudron diagram for the system Cu-Fe is shown. From this representation it is possible to make a prediction for required oxygen potential during slag reduction and to determine when metallic iron could appear in the melt system. As can be observed in this diagram, it is possible to reduce copper oxide at very low CO pressures in the gas phase. However, as copper oxide activity decreases, possibilities for reduction also decreases.

If we consider a FeO activity in the slag, close to 0.6, which corresponds more or less to a saturated fayalite slag, it is necessary to have a copper oxide activity of $1.4 \times 10^{-4}$ to ensure the same oxygen potential value both for liquid metallic iron and copper. After which, a liquid iron alloy, containing dissolved copper will appear.

**Final remarks**

- Copper slags have important amount of components susceptible to be concentrated using different metallurgical techniques and methods, such as magnetic or gravimetric. Once components are separated, hydrometallurgical and pyrometallurgical processes could be employed to obtain final products.
- Main components of non ferrous slags are copper, iron oxides, silica and sometimes precious metals and molybdenum, as has been detected in Chilean slags.
- Slags, as other important wastes today, occurring in copper industry, must be considered as a new mineral resource, which conceptually agree, with the philosophy of a clean production.
- Chile has a particular situation because of the large amount of slags produced, almost 4.0 millions of tons/year, and with and historically accumulation of around 50 millions tons.
- Copper smelters have a great problem today because of the final destination of slags. Smelter plants must consider additional cost of transporting this material far from sites of generation. Thus, the utilization of slags in other productive processes is not only good business, but also gives an environmental solution to the copper mining industry.
- There are several alternatives of slag processing proposed in the present project. However, the best option will be choose after a technical-economic evaluation.

**Acknowledgements**

Authors acknowledges CONICYT (Comisión Nacional de Investigación Científica y Tecnológica, in Chile), for financial support given by FONDEF Project No. D02I1159. Also Chilean smelter plants as well as government institutions participating in this project are acknowledged.

**References**

1a. Waste treatment and environmental impact in the mining industry (Sanchez, M., Vergara, F., Castro, S..


7. Comisión Nacional de Investigación Científica y Tecnológica, CONICYT, FONDEF Project No. D02I1159 ‘Obtención de subproductos con valor comercial a partir de escorias piro metallúrgicas provenientes de fundiciones de concentrados de cobre de la gran minería en Chile’, 2002.


13. RIVEROS G. and WARCZOK A. Rol de varios fenómenos físico-químicos en limpieza de escoria, 51ª Convención Anual del Instituto de Ingenieros de Minas de Chile, 27–30 de Septiembre del 2000, Santiago, Chile.


