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Chapter

Copper Overview: From the Ore to the Applications – A Case Study of the Application of Concentrated Solar Energy to the Treatment of Copper Metallurgy Slags

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Abstract

Copper is a metal that is widely used in different applications mainly due to its thermal and electrical conductivities, together with its corrosion resistance, particularly when it is alloyed. This chapter intends to be a summary of the copper metallurgy: from the historical aspects and mineral deposits or statistics to the different technologies used to produce metallic copper together with the distinct applications (of copper and copper alloys). Environmental issues are deeply rooted in industrial policies to improve the recovery of the metal as well as to minimize the residues generated in the process, which are a problem from the environmental point of view but also from the economic standpoint. Therefore, this document concludes with a research work carried out with the aim of treating copper slags with concentrated solar energy to recover valuable elements from these slags, as iron and copper. Results from this investigation suggest that solar energy could have an enormous potential in the copper metallurgy.

Keywords: copper slag cleaning, copper metallurgy, electrowinning, flash smelting, copper applications

1. Introduction

Copper has been associated to the human history from the moment when it was discovered in native state. It was the first metal used by humans and the second most used after iron through the ages. The name "copper" derives from the Latin word "cuprum", and this word comes from the Roman name of the island Cyprus, where copper was extracted in that period. Nevertheless, there is a historic period known as the Chalcolithic or Copper Age, also termed as the Eneolithic or Aeneolithic, now

regarded as part of the broader Neolithic, where copper was used for utensils, ornaments, tools, and weapons before the Roman Empire appearance. In the Chalcolithic period, copper predominated in metalworking technology and can be defined as a transitional period between the Neolithic and the Bronze Age, where humans discovered that by adding tin to copper, it was possible to create bronze, a metal alloy harder and stronger than either component. Anyway, the utilization of copper significantly increased in the nineteenth and twentieth centuries with the spread of the electricity utilization. Nowadays, approximately 50% of the copper production is employed in the electric power industry and around 25% in construction. The main copper alloys are: brass (Cu-Zn), bronze (Cu-Sn), and cupronickels (Cu-Ni) or aluminum bronze (Cu-Al), widely used in the naval industry and in several piping applications due to its corrosion resistance [1].

The chemical element copper is a reddish metal at the head of group IB in the periodic table, with oxidation states +1 and + 2. Its symbol is Cu; atomic number, 29; and atomic weight, 63.546. The physical properties of the copper depend on the purity as well as on the ore and on the process used to obtain it. This way, impurities in solid solution or segregated phases at the grain boundaries due to the treatment of the metal can have a relevant influence on the properties of the metal. Dislocations or substitutional solid solutions have a significant influence on the thermal and electrical conductivities of the copper, on the plastic behavior as well as on the corrosion resistance. This way, high-purity copper is very ductile; although work hardening increases the hardness and the resistance while the annealing reduces the hardening (elements in substitutional solid solution play the same role). Pure copper can be hot worked, without brittleness, but the resistance at high temperature is poor. Several impurities produce this deterioration of the resistance: S, Bi, Sb, Pb, and Se. The electrical conductivity of copper is the highest among the metals after silver (0.6% of the electrical conductivity of this metal). Cu (2+) is the most stable state but above 800°C, Cu (1+) is more important, which is relevant in pyrometallurgical processes. Copper is a relatively noble element as it can be deduced from its high potential of standard reduction. It gets covered with a thin layer of cuprous oxide under dry air at room temperature. At high temperature (under air), cuprous oxide is first formed but cupric oxide appears later [1]. In the ambient atmosphere, copper surface oxidizes with the years and forms a thin layer, decorative and protective, of green color, mainly formed by basic carbonates and sulfates of copper, which is quite typical from the roofs of historical buildings in central Europe (**Figure 1**).

Copper in a dry atmosphere resists the attack of aggressive products although it exhibits great affinity for the halogen elements and sulfur. Non-oxidizing acids (sulfuric, hydrochloric, and other diluted organic) badly attack the copper. Copper is soluble in oxidizing acids such as nitric and chromic, and in non-oxidizing (sulfuric) having an oxidizing agent (such as oxygen or hydrogen peroxide). Pure water does not corrode copper, but sea water produces a moderate attack. Sulfides are attacked in hydrometallurgy using solutions of ferric salts. Regarding alkaline solutions, there is passivation and the attack at acid pH requires great potential. Oxygen solubility in liquid copper has certain importance. SO_2 dissolves in liquid copper and forms sulfides. Hydrogen is soluble in liquid copper and also remains dissolved after the solidification, being the quantity controlled by reaction with the oxygen (forms water vapor that evaporates and generates residual porosity). Hydrocarbons do not, in general, react with the copper except acetylene. **Table 1** collects the values of several important physical and chemical properties of the copper [1].

Figure 1.
Greenish roofs made of copper and covered with a layer of basic carbonates and sulfates of copper.

Property	Value					Property	Value
Density (g/cm^3)	9.0981–5.7385·10^{-4}·T (theoretical) 8.96 (99.999% Cu) at 20°C (pure) 7.99 at 1083°C (liquid)					Young's modulus (GPa)	100–120 (annealed); 120–130 (cold work)
Melting point (°C)	1083					Elongation (%)	30–40 (annealed); 3–5 (cold work)
Boiling point (°C)	2595					Tensile strength (MPa)	200–250 (annealed); 300–360 (cold work)
Latent heat of fusion (J/g)	211					Brinell hardness (HB)	40–50 (annealed); 80–110 (cold work)
Latent heat of volatilization (J/g)	4.813					Electron configuration	[Ar] 3d^{10}4s^1
Average specific heat (J/g·K)	0.385					Crystalline system	Face centered cubic
Thermal conductivity (W/m·K)	T (°C)	−100	0	20	100	200	Isotopes	^{63}Cu (68.94%) and ^{65}Cu (31.06%)
		435	398	394	385	381		
Electrical conductivity (MS/m)	T (°C)	−100	0	20	100	200	Ionic radius (nm)	(+1): 0.096; (+2): 0.069
		110	60	58	44	34		
Magnetic susceptibility (cm^3/g)	−0.085·10^{-6} (20 °C)					Standard potential of reduction (V)	Cu^{2+}/Cu^0:+0.338; Cu^{1+}/Cu^0:+0.512
Coefficient of thermal expansion (1/K)	16.9·10^{-6} (0–100°C)					Electronegativity	1.9

Table 1.
Physical and chemical properties of the copper.

2. Deposits, minerals, and trends

First copper utensils, ornaments, tools, and weapons were manufactured with casted native copper, but soon other techniques were applied to use other copper sources. In this line, around 80% of the copper that is mined nowadays comes from low-grade ores containing 2% or less of Cu. In this way, even when the copper sulfides metallurgy is relatively recent, it is possible that a few centuries BC metallic copper was obtained from a matte by means of repeated roasting and smelting cycles. This method was applied for centuries, and it was not until the 19th century when the reductant capacity of sulfur was considered. Anyway, before starting with the copper metallurgy, it is convenient to introduce the main copper minerals because they define the process that is nowadays used to produce metallic copper. In fact, copper content in the Earth's crust reaches 70 ppm. This way, more than 160 minerals that contain copper are known but only two main families have importance: oxidized ore (cuprite, Cu_2O; tenorite, CuO) and mainly sulfide ores (chalcopyrite, $CuFeS_2$; bornite, Cu_5FeS_4; chalcocite, Cu_2S). Deposits are mined when the ores contain 0.5% Cu in open-pit mining and 0.7–6% Cu in underground mining. However, significant research is appearing in the field of complex copper ores due to the increasing demand and the potential depletion and decline of good copper ore grades. Low-grade sulfide ores are subjected to concentration operations, which include flotation, to obtain dry concentrates of around 30% of copper with 10–200 μm of grain size [1]. Within this context, it is possible to mention Velásquez-Yévenes and Lasnibat's research [2] about the simultaneous recovery of copper and manganese from "exotic-Cu" deposits in Chile, characterized by the refractoriness to dissolution under acidic and oxidative conditions, or the research of Godirilwe and collaborators about the extraction of copper from complex carbonaceous sulfide ore, characterized by their mineralogical complexity and impurities of organic carbon and carbonates [3]. Other research in this line that can be mentioned is that of Corin and coauthors about complex copper ore (sulfide, oxide, and mixed) in Zambia [4], or Liu and researchers that reported the beneficiation of complex copper oxide ores rich in malachite [5] or the research of Hu et al. about low-grade copper ores with high contents of oxide ore and carbonate gangue (malachite, chrysocolla, chalcopyrite, and chalcocite with gangue minerals as quartz, limonite, calcite, and dolomite) from Yunnan province in China [6].

Porphyry copper deposits are currently the largest source of copper ore. The copper reserves are estimated in 2021 in 880 Mt. (Million tons) according to the United States Geological Survey. Half of these reserves are concentrated in five countries: Chile (200 Mt), Australia (93 Mt), Peru (77 Mt), the USA (48 Mt), and China (26 Mt). Regarding the production/demand of copper, this has grown since the eighteenth century, particularly in the last decades: 10000 tons in 1700, 18,000 tons in 1800, 450,000 tons in 1900, 2.5 Mt. in 1950, 4.5 Mt. in 1960, 7.3 Mt. in 1970, 9.3 Mt. in 1980, 10.9 Mt. in 1990, 15.1 Mt. in 2000, 19.1 Mt. in 2010, 23.1 Mt. in 2015, and 25.3 Mt. in 2020 (year with production significantly affected by the COVID-19 pandemic situation; the estimation for 2021 was 26 Mt). These values refer to the total consumption/production of copper, but it is important to make a distinction between copper mine production and refined copper. This way, approximately 80% of the copper produced worldwide comes from copper extracted from mining operations. Regarding the principal mine copper producers, the main countries are (2021): Chile, 5.6 Mt.; Peru, 2.2 Mt.; China, 1.8 Mt.; USA, 1.2 Mt.; Australia, 0.9 Mt. Regarding the main refinery copper producers of copper, it is possible to indicate (2021): China, 10 Mt.; Chile, 2.2 Mt.; Japan, 1.5 Mt.; the USA, 1 Mt.; Germany, 0.63 Mt.; Australia, 0.45

Mt.; Peru, 0.35 Mt. With respect to the price, the minimum price in 10 years was reached in December 2015 (4577 $/ton) and March, 2020 (4789 $/ton, coincident with the quarantine period resulted from COVID-19), while the maximum price in 10 years was reached in March 7, 2022 (10,729 $/ton, after the Russian invasion of Ukraine).

Aligned with the above-mentioned questions, the equilibrium between the supply and the demand of raw materials or semifinished and finished products is almost unattainable. The reasons of this disequilibrium can be explained by an irrational gathering of raw materials, a sanitary problem (i.e., COVID-19), or military reasons (i.e., Russian invasion of Ukraine). Basic resources (materials, energy, and food) are the first resources in being affected in one or other manner by the distortions of the markets, and this has a significant impact on the development of the poorest countries and regions, in the growth of emerging countries and regions and in the sustainability of developed countries and regions. In this line, countries are identifying strategical minerals or elements whose scarcity would have a significant impact on the chain value. Copper is one of these elements. This metal has still enormous importance in the market despite of its utilization for hundreds of years. In fact, it has gained significant interest in the last centuries due to the electricity market and, it will probably attract more interest with the development of both the sustainable methods of producing electricity and the electric vehicles. In this context, considering the data of the National Renewable Energy Laboratory (NREL) of the USA, 0.7–1.8 tons of copper and 110 tons of steel are required for each MW of installed wind energy [7].

In general, it is important for the beneficiation of the basic resources, particularly copper, to study the evolution of the price of the raw materials in a period of time comparable to the proposed duration of the project (development, exploitation, and conclusion). For this reason, it is realistic to analyze the copper market from 1980 [8]. The copper price in 1980, which approximately coincided with the end of the second oil crisis, was 2400 $/ton, while in 1995 it was not far from the price in 1980: 2976 $/ton. However, the irrational development of the real-estate market in the period 1995–2010 made the copper price to grow 2.2 times, while in the period 1980–1995, the growth was only 0.24 times. After the real-estate bubble, the price descended to a minimum of 4553 $/ton in 2015 and started to progressively grow up to an average value around 6000 $/ton before another minimum coincident with the COVID-19 lockdown in March 2020 in 4789 $/ton. The copper price has sharply grown since that minimum until reaching values never seen before, after the Russian invasion of Ukraine (>10,000$/ton). It is possible to think, as it is indicated by Brinded [9], that the copper market is mad. Maybe this term is not the most adequate because it sounds better to say that the copper market is in crisis. There is not a single reason to justify this situation, but it is necessary to consider several variables in the implementation of a mining project: the price of the metal in the London Metal Exchange, the tons of proven metal reserves in the deposit, and the grade-concentration of the metal in the proven reserves. Therefore, it seems not reasonable to start a mining project considering only the highest prices in the market but an average value over a long period (and different scenarios) together with the other variables indicated in this paragraph, as otherwise, for instance, projects started under the current copper prices could lead the mining project to fail whether the prices descend. Moreover, the project should consider its complete duration (from the early stages of reserves estimation to the land rehabilitation after the end of the project). Therefore, economic resources obtained from the sale of the metal in the market are approximately distributed as follows: 14% for the exploration, 44% for the mining-exploitation-concentration operations and environmental conservation, 23% for the extractive metallurgy, 6% for general costs

and management of the project, and 13% of economic profit, for successful project implementation, based on previous works within this field and considering the economic evaluation of mine implementation projects [10, 11].

3. Copper metallurgy and refining

3.1 Introduction

The primary source of Cu is porphyry deposits. The treatment of primary copper ores by the pyrometallurgical process is responsible for about 80% of the world's copper production [12]. However, the production of copper taking advantage of copper sulfides' characteristics is relatively recent. The production of copper in the Middle Age (as it is collected in *De Re Metallica* of Georgius Agricola) was based on the Mansfeld process, which involved seven operations of roasting and melting. First, the slagged gangue was separated from the matte with low metallic content, and then, this was enriched by concentrating smelting, carrying to the slag, by oxidation, the iron content. The enriched matte was dead roasted to obtain an oxide that was treated by reducing smelting to obtain black copper, which was later refined. It was in 1700 when the Welsh process was introduced, which significantly modified the method of obtaining copper. It consisted of 10 operations at the beginning, although it involved 6 or 7 stages in 1830. The main difference was the extensive utilization of the roasting process or double decomposition process, where sulfur was used as reductant reagent. At the beginning of the Modern Age, Germany was the leader in copper production, but in 1800 England became the biggest copper producer. Chile became the first copper producer in 1859 and, from that moment, this country is the biggest copper producer in the world. Even when, as we have already seen, copper has been produced for several centuries, the greatest developments in technique are from the last centuries: the application of air/oxygen blowing as in the Bessemer converter, the development in Finland of the flash smelting process after the World War II, industrial electrowinning in the second half of the nineteenth century or the discovery of the differential flotation of sulfides also in the second half of the nineteenth century. These developments, as well as the applications of copper in construction and electricity, have made this metal one of the five most produced worldwide [13].

3.2 Principles of the process used to obtain the matte

Pyrometallurgical copper smelting processes are based on the principle of partial oxidation of sulfide concentrates [1]. The methods based on the total oxidation of sulfides with posterior reduction of the metal oxide, without formation of a copper matter, are generally not used due to both the high consumption of combustible, the formation of copper-rich slags and the obtaining of crude copper with high level of impurities. This way, the smelting of sulfide concentrates, partially roasted or without roasting, with the addition of impurities, produces two immiscible phases: one heavy containing most of sulfides that is known as matte; other oxidized and ferrous is known as slag. The reactions of oxidation of the sulfur of sulfides and iron, both exothermic, produce the matte with adequate composition and it is possible to use the heat of the reaction if the suitable technology is used. The formation of the slag, by reaction of the iron (II) oxide with the silica, which is used as a flux to form fayalite

(main component of the slag) and separate the iron from the matte, is also exothermic. The reactions involved in the formation of the matte are described as follows:

$$4CuSFeS(s) + 5O_2(g) \leftrightarrow 2(Cu_2S \cdot FeS)(dis; matte) + 2FeO(s) + 4SO_2(g) \qquad (1)$$
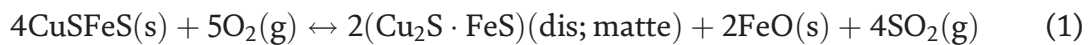
that is an exothermic reaction, as the next one:

$$2FeO(s) + SiO_2(s) \leftrightarrow 2FeO \cdot SiO_2(dis; slag) \qquad (2)$$

The most important equilibrium, between the phases (matte and slag), is the following one, which is displaced to the right side of the equation:

$$Cu_2O(dis; slag) + FeS(dis; matte) \leftrightarrow Cu_2S(dis; matte) + FeO(dis; slag) \qquad (3)$$
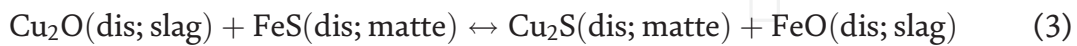
The presence in the matte of liquid iron sulfide reduces the iron (III) oxide to iron (II) oxide:

$$3Fe_3O_4(s) + FeS(s) \leftrightarrow 10FeO(s) + SO_2(g) \qquad (4)$$
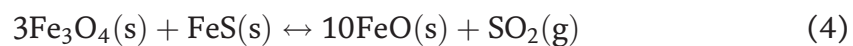
The previous reaction can be used to eliminate part of the magnetite, with the presence of silica because the magnetite is detrimental for the operations in the furnace due to its high melting point (>1500°C), which increases the viscosity of the slag and increases the quantity of copper in the slag.

Therefore, the process used to obtain the matte is a copper concentration process in this phase. There are several elements that accompany the copper that are essentially reduced. Thus, calcium, magnesium, and aluminum go directly to the slag, while precious metals go to the matte. The other metals, Ni, Co, Pb, Zn, As, Sb, Bi, etc., distribute between both phases or, separate with the gases of the furnace. The matte is fundamentally a mixture of sulfides in the pseudo binary Cu_2S-FeS system. The density of the matte is in the range of 4.9–5.3 g/cm^3 depending on the state (liquid or solid) and the copper content. On the contrary, the slag has a density 1 g/cm^3 lower and comprises a 30–40% of iron as oxides and 25–40% of silica, mainly as iron silicate (fayalite). The smelting process involves an almost complete separation of the matte and slag due to the different densities and the different nature of the chemical bonding (covalent in the matte and ionic in the slag). Some technologies of fusion (reverberatory furnace) produce slags with 0.6% of copper and others, as the flash smelting Outokumpu (introduced by this Finnish company) [1], produce slags with 1.2% of copper that must be treated by either reduction in an electric furnace with additions of carbon and pyrite or flotation after milling.

3.3 Traditional smelting of copper sulfides

The most traditional form of obtaining copper in the fifties of the twentieth century consisted in roasting the concentrates of sulfides and melting the products in reverberatory furnaces, sometimes in electric furnaces and less frequently in shaft furnaces. A matte was obtained, which was later subjected to oxidation in Pierce-Smith converters. The main advantage of this technology is the production of slags that can be directly sent to controlled landfill. Within this group of technologies, it is also possible to mention the Noranda and Teniente processes [1], which in fact are big converters adapted for the smelting to obtain the matte. In these technologies, the

concentrate is mixed and flows in a turbulent bath matte/slag; additionally, the Fe and S of the concentrate oxidize to form a rich matte, a slag that cannot be disregarded, and a gas with high SO_2 content. The matte (70–75% Cu) is sent to the converter to obtain blister copper. In the particular case of the Noranda process, it was set at the beginning as a continuous process to directly produce blister copper, but it failed. The idea/objective of obtaining copper in a single stage was one of the industrial research objectives for years, as we are going to see later. Returning to the Noranda process, the system involved the simultaneous presence of three phases (slag, matte, and metal) and, it was not possible to achieve a good recovery of copper from the slag. The metal was obtained with great contamination and, therefore, several problems arose during the electrowinning.

3.4 Flash smelting

The flash smelting is the dominant technology in the market. It can be autogenous or not, but the main characteristic is the rapidness of the smelting process resulting from the utilization of a burner with preheated air, enriched with oxygen, or with industrial oxygen. The process will be autogenous if the following condition is accomplished: the partial oxidation of sulphides generates enough heat to melt the matte and the slag and have them as separated phases in the furnace (due to density difference). Heat is usually provided to ensure the reactions matte-slag and the separation of both phases. In flash smelting, the stages of roasting and oxidizing smelting happen simultaneously taking advantage of the heat generated in the process. The only autogenous technology is the INCO process that uses industrial oxygen and a design of the furnace that allows copper slag with 0.7% Cu. The other technologies have the disadvantage of high copper content in the slag due to the high oxidizing environment of the process and the high quantities of magnetite in these conditions (which is in solid state when it is in excess), which makes it almost impossible to empty the slag from copper using the Eqs. (3) and (4).

The Outokumpu process of flash smelting is the most important technology to produce copper (8 of 20 biggest copper smelters according to the ICSG Directory of Copper Mines and Plants use this technology). This process was developed in Finland
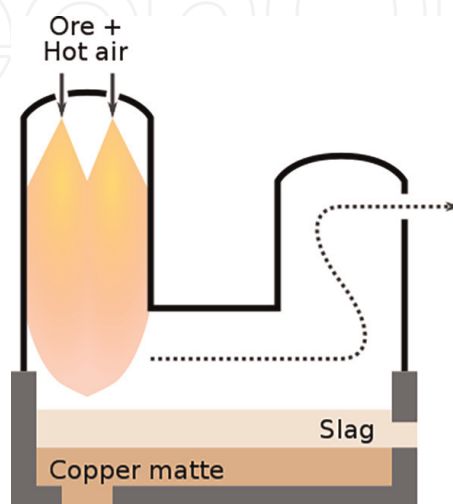
Figure 2.
*Scheme of the Outokumpu smelting process (*source: *Wikicommons).*

in the fifties of the last century and has great productivity and easy control. The scheme of the process appears in **Figure 2**.

The furnace can be divided into three sections [1]: tower, for the partial roasting and smelting of the dry concentrate in suspension; horizontal zone, where the matte and the slag are separated; and, chimney, for the exit of gases that end in the acid plant after pretreatments to use the heat and remove the particulate matter. The process in the tower is almost autogenous but the heat for the separation of the matte and the slag is provided by gas or fuel. The copper content in the slag is around 2% of copper, which involves a posterior treatment in an electric furnace with pyrite and carbon to reduce the copper content in the slag (the slag can be sold as abrasive or material for roads). The hot gases collected in the process are used in a boiler and the powders that they contain are collected with mechanical separators or electrostatic filters. These powders (5–10%) are recycled again in the furnace or treated depending on the concentration of volatile elements.

Other technologies of flash smelting are the INCO process, cyclonic smelting KIVCET, Isasmelt process, Vanyukov process, and Contop process.
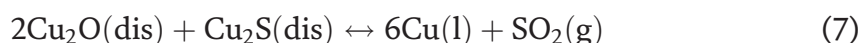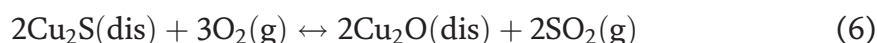
3.5 Conversion

Conversion is the process where the matte generated in the smelting process, which is in molten state, is treated by injecting oxygen to the melt, mainly in Peirce-Smith converters. The process consists of two stages:

• The first is known as "slagging stage" and a phase formed essentially by copper sulfides, white metal, where there are less than 1% of iron sulfides, is obtained. The converter is filled again with copper matte to obtain more white metal by oxygen injection. The process is repeated several times (5 or 6 [1]) until the moment when the converter is filled with copper sulfide. The main reaction of this first stage is:

$$2FeS(dis; matte) + 3O_2(g) \leftrightarrow 2FeO(dis; slag) + 2SO_2(g) \tag{5}$$
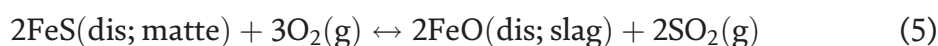
The ferrous slag of the first stage is separated, normally, by addition of silica (fayalite) as in the Eq. (2).

• The second stage allows obtaining blister copper by oxygen injection to the white metal. The reactions in this stage are:

$$2Cu_2S(dis) + 3O_2(g) \leftrightarrow 2Cu_2O(dis) + 2SO_2(g) \tag{6}$$

$$2Cu_2O(dis) + Cu_2S(dis) \leftrightarrow 6Cu(l) + SO_2(g) \tag{7}$$

Even when there is 1% of FeS at the end of the first stage [1], it is impossible to avoid the formation of magnetite due to the high oxidizing potential inside of the converter and the inefficiency of the reaction indicated in Eq. (4) to destroy the magnetite. For that reason, the excess of magnetite crystals (with high melting point) produces a viscous slag that involves the pass of significant quantities of copper oxide to the slag (15% Cu). This way, converter slag must be recycled.

The conversion stage is used, apart from to eliminate sulfur and iron, to refine the content in metallic elements. Nobler metals as nickel and cobalt remain in the blister

copper. On the contrary, the slag enriches in zinc, although part volatilizes during the process. As, Sb and part of the Sn, Pb, and Bi can be found in the particulate matter collected before the chimneys (the rest remains in the slag, and only very small quantities in the metal, mainly the bismuth). Finally, blister copper contains 1% S, 0.5–0.6% O and traces of the above-mentioned metals. The conversion process is highly exothermic, making the process autogenous, which allows the charge in the converter of scraps, cemented copper or even concentrates to control the temperature of the process. Therefore, recent investigations in this line are focused on the application of mathematical modeling to minimize copper losses [14] and to increase the energy efficiency of the process [15].

3.6 Flash smelting to produce copper

We have already pointed out that one of the objectives in the copper industry has been to obtain blister copper in a single step. The process required to use air highly enriched with oxygen, which resulted in installations with low capacity of operation because of the rapid deterioration of the tuyeres. Different technologies were proposed in this line, as the Noranda process as it was already pointed out, or the Mitsubishi, which is not based in a single step, among others. Mitsubishi process consists of three interconnected furnaces (smelting furnace to produce the matte, furnace to recover copper from slags and converter furnace) and is installed at least in Birla Copper (Dahej) in India according to the ICSG Directory of Copper Mines and Plants. Further information about the Mitsubishi process can be found in Ref. [16].

3.7 Copper hydrometallurgy

This route of production of primary copper accounts for approximately 15% of the total world production. This route is particularly useful for low-grade ores or low-grade sulfide residues. This is because oxide ores are very limited worldwide. The copper hydrometallurgy is very extensive. Here we present a summary of the most common techniques (further details about copper hydrometallurgy can be found in the reference [17]). Lixiviation can be applied: in situ to low-grade ores, in spoil tips for piled-up material, in boxes by percolation for fine-grained material, or in stirred reactor with or without pressure or temperature for fine-grained material. As leaching agents, it is usual to employ diluted sulfuric acid (for copper oxide ores, carbonates, basic sulfates, and silicates), iron (III) salts solutions prepared or formed *in situ* in presence of oxygen during the lixiviation process from iron (III) sulfate (these solutions, the same as chlorides, are oxidizing and are adequate for copper sulfides), chloride solutions with an oxidizing agent (which are adequate for copper sulfides) and ammonia solutions with ammonia salts, as the ammonium carbonate, for oxidized ores as well as for native copper in presence of carbonate gangue. Rich solutions obtained in the lixiviation process are filtered and sometimes purified to remove polluting dissolved elements. Finally, copper is obtained by cementation, electrolysis, or precipitation of compounds. Cemented copper is melted and fire-refined and subjected to electrowinning. The electrodeposit is sold or melted in ingots because it has its own market (99.9% Cu), or it is subjected to electrowinning. The application of hydrometallurgy in the recovery of wastes is gaining interest, particularly to treat waste that is generated in large quantities in the copper pyrometallurgy as the copper slag. Within this context, Mussapyrova and colleagues [18] reported the copper

selective leaching from mechanically activated copper smelter slag with copper recovery of 87.3% and maximum copper selectivity of 97.9%.

3.8 Fire refining and electrowinning

The refining traditionally involves two stages: fire refining and electrowinning. The product obtained at the end of the first stage usually has 99.9% Cu, which can be insufficient for most applications and electrowinning is required to achieve a purity of 99.995% [1], required for electrical applications. It is possible to obtain a purity of 99.9999% Cu by repeated electrowinning processes or zone melting. This quality is used in research or electronics.

Fire refining (applied in the case of blister copper or in the products of the hydrometallurgical route) consists in eliminating the sulfur (to thousandths of percentage point) and reducing the oxygen content below 0.1%, by reduction, until having a free flat surface of metal resulted from the compensation of the volume of the pores by release of water vapor and gases retained in the metal. The equilibrium sulfur-oxygen in the blister copper can be expressed as follows:

$$S(dis; metal) + 2O(dis; metal) \leftrightarrow SO_2(g) \tag{8}$$
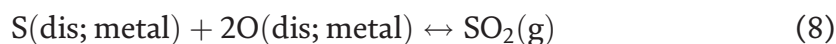
with an equilibrium constant of:

$$k_{eq(Eq.8)} = \frac{[SO_2]}{[O]^2 \cdot [S]} \tag{9}$$

The value of this constant between 1200 and 1300°C is 25, which for a pressure of SO_2 of 0.1 atm gives $[O]^2 \cdot [S] = \mathbf{4 \cdot 10^{-3}}$. This implies that for a sulfur content of 0.02%, the oxygen content would be around 0.5%, and in the case of 2 ppm of sulfur, copper would admit oxygen content above 1%. However, the part of the copper oxidizes to copper (I) oxide during the blowing stage, being dissolved in the metal, and this phase is a selective oxidizing agent as it is expressed in the following equation:

$$S(dis; metal) + 2\,Cu_2O(s) \leftrightarrow 4Cu(l) + SO_2(g) \tag{10}$$

Figure 3.
Copper anodes for the electrowinning process (source: Wikicommons).

The fire refining process is carried out in modern cylindrical furnaces (and sometimes in reverberatory furnaces) and at the end of the process high copper content slags are obtained, which are recycled, and the metal with very low sulfur and oxygen content, which is casted in anodes for the electrowinning process (**Figure 3**).

More than 80% of the world's copper production is refined by electrowinning, which yields high electrical conductivity copper and the separation of the impurities (the precious metals can be recovered at this stage). The process is carried out in cells with 50 g/l of copper in sulfuric medium at temperatures of around 60°C [1]. Periodic purges of the electrolyte are required to eliminate the metals that could compete with the copper in the electrolysis process (As, Sb, Bi, Ni, Co, and Fe). Nobler metals than the copper end in the anodic lodes. The contamination with silver is controlled with small additions of chloride. Sulfur, selenium, and tellurium fall to the anodic lodes, the same as the lead and tin because of not being soluble in sulfate medium. The purification of the electrolyte is carried out by crystallization of the copper pentahydrate sulfate salt and posterior precipitation of the metals by pH control or by means of additives (it is also possible to precipitate the competing metals in an impure cathode that is later recycled in previous stages). The copper cathodes have a purity of >99.99% Cu, which is the electric quality as we will describe later. Anodic slime represents a quantity <1% in weight but they contain precious metals, so they are periodically collected from the bottom of the cells. They are later filtered and dried and subjected to treatments to recover the valuable metals: initial treatments allow to solubilize the copper, later selenium and tellurium are recovered and precious metals finally are melted in an alloy that is known as bullion or doré. Further details about the anode slime are available in Ref. [19].

3.9 Copper foundry

Copper cathodes can be sold as produced but it is quite common to melt the metal to obtain semifinished products. This way, cathodes are melted in furnaces where the metal is cleaned, and alloying elements are added to finally cast the metal. There are different processes of casting: semicontinuous casting, continuous casting, or casting in ingot molds. Different types of furnaces are used for this purpose, but combustibles must be free of sulfur to avoid the contamination of the copper with this element [1], with a maximum of 10 ppm of sulfur because greater contents have a noticeable influence in the mechanical properties of the copper. Semifinished copper products include wires, strips, and rods, among others, and for some specific applications, copper powders are gaining interest. Powders are manufactured from aqueous solutions by cementation or precipitation with hydrogen at high pressure, or also by atomization or by electrolytic method. Finally, three different copper qualities are defined [20]: Refined copper or electrically refined cathode (Electrolytic-tough Pitch Copper, ETP): 99.99% Cu with $0.03 \pm 0.01\%$ Cu_2O, which can be easily worked and has high electrical conductivity (100% IACS) but poor weldability (80% of the world copper production is from this quality).

- Phosphorus deoxidized copper: almost free of oxygen and is produced by the addition of reductant reagents. It can be welded. The electrical resistivity can be increased due to the presence of phosphorus, being this copper (0.04% P) used in applications where electrical conductivity is not required.

- Copper free of oxygen (Oxygen-free copper [OFC], or oxygen-free high thermal conductivity [OFHC]): obtained whether molten copper is kept under an inert or reductant atmosphere. This allows an oxygen content <0.001%. It is used in electronics due to the high electrical conductivity.

Finally, there is another quality of copper obtained by electrical recovery: 99.9%, with poor applications, maybe in some alloys. Research in this line is gaining interest in order to minimize the waste. For instance, the recovery of copper from electric cable waste is derived from the automotive industry by corona-electrostatic separation (99.8% Cu) [21] or waste printed circuit boards utilizing recycling of leachate (99.9% in electrowinning) [22].

4. Applications of copper

Copper, and copper phases, has many different applications due to the excellent properties. Here we present a summary of the main traditional uses of copper. In this line, 50% of the copper is employed because of its excellent electrical conductivity, particularly in low-voltage applications (electric machines, including engines or transformers, among others). Another important application of copper is in semiconductor interconnects in integrated circuits [23].

Copper also exhibits high thermal conductivity and, therefore, it is used for vessels and heat exchange tubes. Other of the main applications of copper is in chemistry or feeding industries, as well as in automotive or naval industries due to the corrosion resistance, particularly when it is alloyed as brass (Cu-Zn), bronze (Cu-Sn), and cupronickels (Cu-Ni) or aluminum bronze (Cu-Al).

Copper is also used in the construction industry for conductions and coatings, and also in appliances, ornamental, and coins. It is also applied in antifriction bearings and several parts of powder metallurgy, and also in the manufacture of ammunition. Copper salts, mainly sulfates and oxides of copper, represent 1% of the world's production. Copper sulfate pentahydrate is used in agriculture to avoid fungi in fruit trees and vegetables due to the efficiency and low toxicity. Soluble copper is also added to feed and food, and also other copper compounds are used as insecticides and preservatives. Metallic copper and some of the copper compounds are used as catalyzers in numerous organic reactions, or as pigments for glass, ceramics, or enameling. Certain copper compounds have applications in the petroleum industry.

We mention here some novel potential applications of copper, copper alloys, or copper phases, as, for instance, complex copper alloys for extreme conditions applications (novel CuCrZrFeTiY alloy for fusion reactor [24]) or bulk metallic glasses [25]. It is also gaining interest due to the bactericidal activity against important human pathogens [26].

5. Environmental issues

Regarding environmental issues, the most relevant points to be considered for action are: control of emissions to the atmosphere, and protection of water and disposal of solid residues. We might indicate here the growing importance of obtaining copper from secondary materials or scraps, as it was already mentioned, in order to reduce the volume of residues and the energy consumption (which is smaller

in the case of recycling copper). In this line, apart from the practice carried out in other metallurgical industries with respect to environmental issues, two points have special relevance: SO_2 emissions and copper slags. In the case of SO_2, this is unavoidably formed in the production of copper during the smelting and conversion, but the final application of this gas is the manufacture of sulfuric acid. The production of sulfuric acid implies cleaning and drying the gases of the furnace followed by the catalytic oxidation of SO_2 to SO_3 and the absorption of the resulting SO_3 by the water to generate H_2SO_4 with 98% concentration. This process is autogenous when we start from gases with 4 vol. % of SO_2 or greater content, bigger contents involve specific treatments. Modern plants of double absorption can even recover 99.5% of the SO_2 at the entrance. The manuscript of Alexander and colleagues about the environmental performance of modern copper smelting technologies is an interesting review about the environmental issues in copper metallurgy [27].

Copper slags are a problem in copper metallurgy due to the large quantity that is generated of this by-product: 2.2–3.0 tons slag for every ton of copper produced [28]. The applications of this residue are very limited since the researchers have still not found a massive utilization for this material [29]. Copper slags have been used as abrasives (polishing and cleaning) for metallic structures [30, 31] and mainly in the building industry: concrete manufactured with copper slag [32]; copper slags as fine particles in concrete manufacturing [33]; copper slag as a replacement for the sand in cement [34]; copper slag as a filler in glass–epoxy composites [35]; and copper slag as a construction material in bituminous pavements [36]. However, due to the high iron and copper contents (>40 wt. % and 1–2 wt. %, respectively), copper slags could become a secondary source for metal recovery [37, 38]. A total of 20 Mt. of primary copper is produced worldwide, and this involves 45 Mt. of slag generated in the process (2.2–3 tons of slag/ton copper [28]), which would represent >20 Mt. Fe and 0.5–1 Mt. Cu yearly sent to controlled landfills. Therefore, copper slag represents an environmental impact [39]: risks of heavy metals lixiviation, a visual impact, and sometimes occupation of cultivable areas. Moreover, research has also focused on the recovery of iron from the slag due to the high iron content in the copper slags: by using coke as a reductant of the copper oxide and the magnetite [40]; by modifying the molten slag with the purpose of promoting the mineralization of recoverable mineral phases and inducing the growth of the mineral phases [41]; by using a method based on coal, Direct Reduction Iron (DRI), and magnetic separation [42]; by means of a process based on aluminothermic reduction [43]; by reduction in an electric furnace with the objective of obtaining a Cu-Pb-Fe alloy [44]; by carbothermal reduction to transform the copper slag into pig iron and glassy material [45]; by irradiation with a microwave as a support of the carbothermal method [46]; or by reduction with coke powders and magnetic separation [47]. In the following section, we present a study about the application of concentrated solar energy to recover valuable metals from copper slags.

6. Case study: Application of concentrated solar energy to the treatment of copper metallurgy slags

6.1 Introduction

The term solar energy is often associated with the generation of heat or electric power. Nevertheless, solar energy, when it is adequately concentrated offers

enormous possibilities in the field of materials science and metallurgy, including the recycling of residues from these industries, because of the high temperatures that can be reached by using this technology (up to 3500 K [48]). In this context, solar energy has been used in metallurgy and materials science for centuries [48]. The legend tells that Archimedes destroyed the Roman army during the Syracuse Siege using mirrors (213–212 BC), although the most traditional application of solar energy in the field of materials was the drying of adobe bricks for the construction of houses. More technical applications appeared during the early Modern period (17th century), when a German mathematician, Ehrenfried Walter Von Tschirnhaus, designed, constructed, and worked with lenses and mirrors to concentrate solar energy [48] and melted iron and obtained ceramics (porcelain). Other researchers worked with concentrated solar energy during the Modern period as Cassini (seventeenth century), who designed a lens with 1 meter in diameter to reach temperatures of around 1000°C and melted iron and silver, or Lavoisier (eighteenth century), who melted iron and approached the melting point of platinum, and also treated metals under special atmosphere such as nitrogen [48]. Anyway, it was after World War II when the investigation in the field of solar energy applications definitely emerged with the construction of the first solar furnace in Mont-Louis (France) in 1949, which was the precursor of the Odeillo solar furnace (Font-Romeu-Odeillo-Via, France; construction from 1962 to 1968; start of operations in 1969, **Figure 4**) under the figure of Felix Trombe, who demonstrated how to employ solar energy to melt high melting point refractory ceramics (alumina, chromium oxide, zirconia, hafnia, and thoria) [48]. Nowadays, there are several installations where it is possible to research within this topic: PSA-CIEMAT (Plataforma Solar de Almería, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, in Spain), PROMES-CNRS (Procédés, Matériaux et Énergie Solaire, Centre National de la Recherche Scientifique, in France), Solar Laboratory at the Paul Scherrer Institute (in Switzerland), Weizmann Institute of Science (in Israel), or National Solar Thermal Test Facility and National Renewable Energy Laboratory (in USA), among others, which have made significant contributions to the development of solar-based metallurgical processes. From these original researchers of Von Tschirnhaus, many other researchers have made significant contributions to the progress in the field of concentrated solar energy applications in the field of metallurgy and materials science. These researchers can be read in the extended review published in 2018 in the journal *Solar Energy* with the title *Concentrated solar energy applications in materials science* by Fernández-González and collaborators [48].

Figure 4.
*Odeillo solar furnace (font-Roméu-Odeillo-via, France).*

Focusing on our research group, the investigation has focused on the: synthesis of calcium aluminates [49], iron metallurgy [50, 51], the treatment of Basic Oxygen Furnace (BOF) slag [52], the production of silicomanganese [53], and transformations in the Ca-Si-O system [54]. The objective of the present Case Study is to present an application of concentrated solar energy in the copper metallurgy: potential recovery of copper and iron from copper slag using solar energy as heat supply for the process.

6.2 Materials and methods

As raw material for experiments, original copper slag from the cleaning furnace was used. It consisted of (wt. %): Fe, 42.82; O, 36.15; Si, 10.36; Al, 3.24; Cu, 1.84; Ca, 1.76; Na, 0.99; S, 0.52; others, 2.32, determined by X-ray fluorescence. X-ray diffraction technique was employed to determine the form in which the crystalline phases of the above indicated elements were: fayalite (Fe_2SiO_4), $85.80 \pm 1.30\%$ in the quantitative analysis; other important crystalline phases were magnetite (Fe_3O_4) and copper–iron oxide (cuprospinel, $CuFe_2O_4$, with Cu^{2+} and Fe^{3+}), $7.90 \pm 1.60\%$ and $6.20 \pm 1.80\%$, respectively, in the quantitative analysis [37].

Tests were performed in a vertical axis 1.5 kW solar furnace located in Font Romeu-Odeillo-Via. The functioning of the solar furnace consists of making solar radiation converge on a small surface (12–15 mm in diameter), called the focal point (where the experimental device is located), using a parabolic concentrator (2.0 m in diameter) and a heliostat that directs sun radiation to the parabolic concentrator. A scheme of the process is represented in **Figure 5**. Several experiments were carried out. They lasted between 15 and 30 minutes, with values of power from 563 to 1409 W.
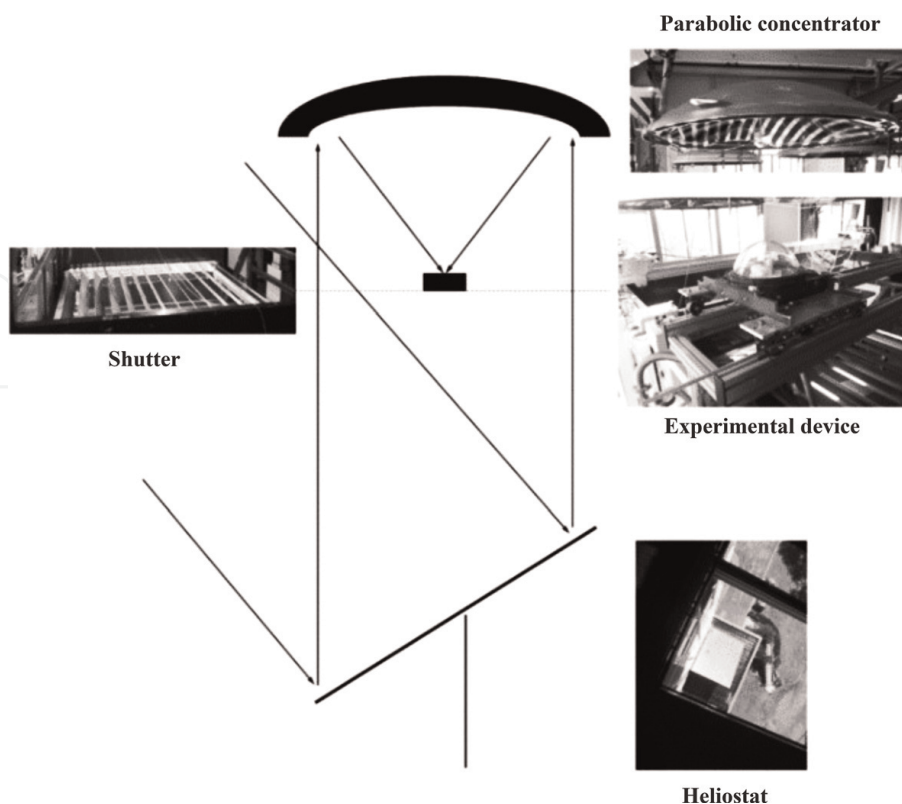
Figure 5.
*Scheme of the equipment used for the experiments [37].*

6.3 Results and discussion

From visual macroscopic analyses of the samples, it was possible to check that the sample became magnetic after the treatment of the slag with concentrated solar energy. Moreover, occluded matte (copper sulfides) decomposed at the temperatures of the treatment as it is deduced from the investigation carried out by Winkel (metallic copper, iron sulfide, and elemental sulfur can be obtained after the treatment of copper concentrates at a high temperature under an inert atmosphere) [55]. This was corroborated by the fact that there was sulfur in the opposite face to the solar beam, which was the result of the decomposition, according to the above indicated mechanism, of the occluded matte under an ambient in this zone characterized by the low oxygen content.

Samples were subjected to Scanning Electron Microscope (SEM) observations, which confirmed the partial transformation of the copper (as sulfides or oxide) into rich nodules of copper (60–85 wt. % Cu), and also the partial transformation of the fayalite ($FeSiO_4$) into magnetite (iron spinel). SEM images can be observed in **Figure 6**.

The average composition of the copper nodules (as those in **Figure 6**) was 65–85 wt. % Cu; 5–10 wt. % Fe; 2–10 wt. % O; <3 wt. % S, while the size was between 5 and 10 µm, although nodules with a larger size were detected in some samples (between 20 and 35 µm).

Samples were subjected to crushing and grinding down to 40 µm. Then, they were separated into two fractions: magnetic and non-magnetic. The ratio of magnetic to non-magnetic was >80 (average value: 83.3625, in weight). Each fraction was analyzed by X-ray diffraction and X-ray fluorescence. The copper concentrated in the non-magnetic phase 3–6.5 times with respect to the initial slag (1.84 wt. % Cu), non-magnetic fraction contained >7 wt. % Cu. The grade in mining is an important factor about how much a deposit is worth, as it was mentioned at the beginning of this manuscript. The average grade of copper ores in the 21st century is below 0.6% Cu for outside mining operations. This would mean that copper slags might become a potential secondary source of copper, particularly if copper could be concentrated using solar energy. Further information can be read in *Recovery of Copper and Magnetite from Copper Slag Using Concentrated Solar Power (CSP)* [37].
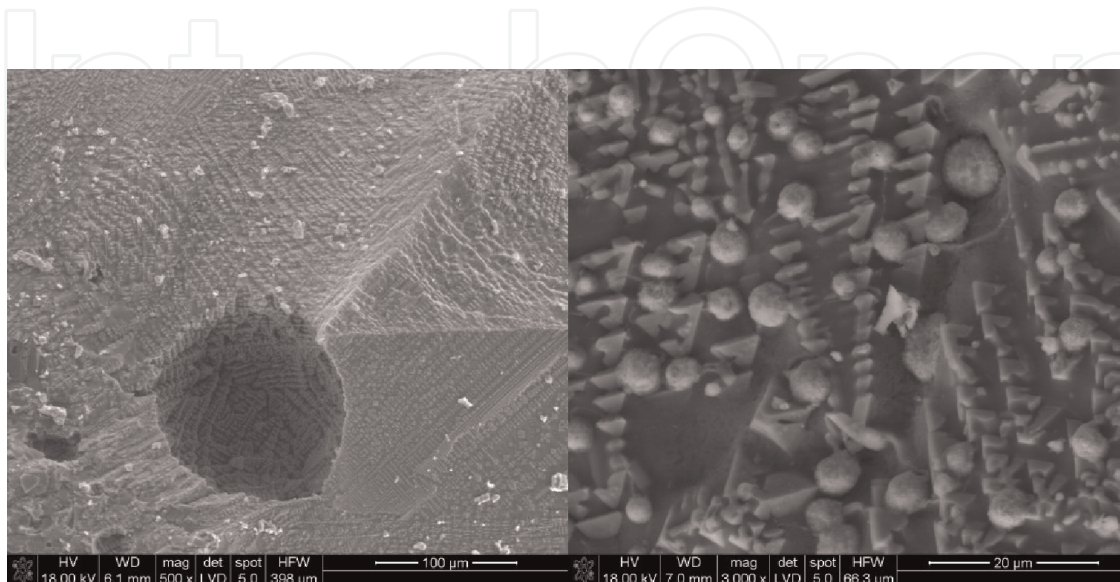
Figure 6.
SEM images of the copper slag treated with concentrated solar energy.

7. Conclusions

This chapter includes a brief review of all the processes used in copper production. The document begins with the introduction of the properties of copper as well as the correlation of the applications with the properties, where it is important to mention the application of copper in electrical and mechanical applications due to its excellent values of thermal and electrical conductivities. The chapter continues with a brief description of the main copper ores, the copper sulfides, which define the subsequent processes that are employed to obtain the metal. The main copper producers are highlighted later. Here it is possible to see the importance of porphyry copper deposits in Latin American countries (as Chile and Peru). However, refined copper is mainly produced in China, Chile, and Japan. Regarding the price of copper, it has significantly increased since the end of the COVID-19 restrictions and has reached the maximum just after the Russian invasion of Ukraine, although this situation could be transitory and copper prices for projects should be based on a long period not in a short period, combined other variables as the proven reserves or the copper grade in the deposit. The process of copper production, including all existing technologies, is described later, from the principles of the matte production to the different qualities of copper that are obtained at the end of the process. The manuscript concludes with a case study about the utilization of concentrated solar energy to treat copper slags in attempts to recover copper and iron from these slags. This document should be seen as an overview of the copper production process.

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