Supplementary Materials: A Review of Carbon Footprint of Cu and Zn Production from Primary and Secondary Sources

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1. Copper Production

Copper is considered the third most important metal for industry after iron and aluminum with a yearly production of 10 Mt. Most of the global Cu reserves are present in Latin America, from where the European Union imports around half of the Cu used [1]. Although the global reserves of Cu in the crust of the Earth are extensive, only a fraction of them is considered economically profitable to extract with currently available techniques.

It has been predicted that the market of Cu will reach 30 Mt in 2030–2040, which is approximately 8% higher than the predicted metal production for the same period [2]. On the other hand, the International Copper Study Group (ICSG) claims that the copper mining capacity will be 26 Mt in 2019 with an expected annual increase rate of 4%. By taking into account the decreasing ore grades, some studies indicate that Cu mining will reach its peak around 2050 [2–4], giving economic incentives to mine secondary sources, while other studies predict that the development of innovative technologies will result in an increase of plant capacity [5]. A summary of Cu sources considered in this review as well as the main production technologies are shown in Figure SI1.

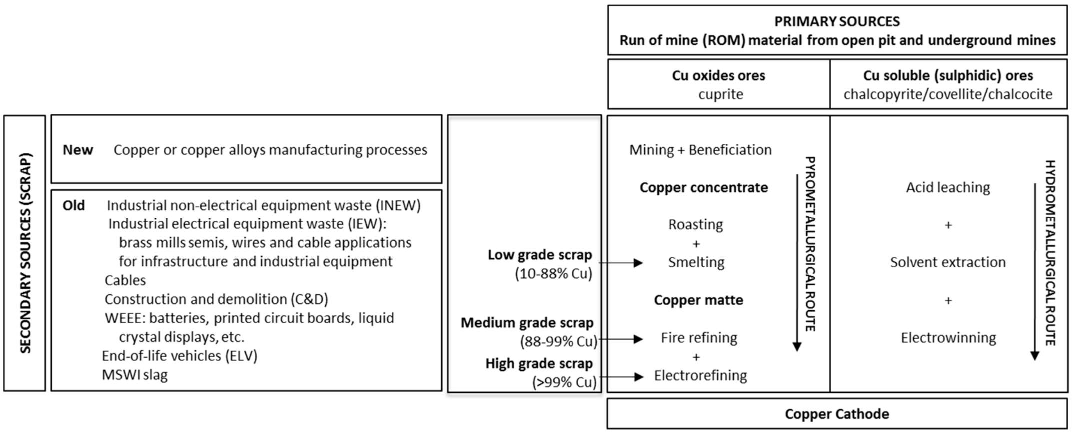

Figure SI1. Summary of Cu sources and main recovery process. Adapted from [6,7].

1.1. Primary Production of Cu

Copper is mined both from open pit and underground mines, however most major production countries mine Cu ores from open pit mines [8]. Cu ores normally occur as either oxides or sulfides and chalcopyrite ($CuFeS_2$) is the source for roughly 50% of the globally mined Cu [9]. Upgrading processes to produce high-grade Cu include the stages of concentrating, smelting and refining [10]. Oxide and sulfide ores with lower copper content are generally processed by hydrometallurgical technologies, which incorporate leaching followed by solvent extraction and electrowinning (SX-EW) steps [5,11,12]. Hydrometallurgical processes are able to treat lower ore grades as well as neutralize and handle easier wastewaters and residues after solid/liquid separation [13].

1.2. Secondary Production of Cu

Copper can be recovered from the majority of its end-products and returned to the production process without loss of quality during recycling. In 1980, the world Cu smelter production was 7500 Gt (300 of each from secondary sources), while in 2015 this figure increased to 18.600 Gt (3300 of each from secondary sources) [5]. In EU countries, the secondary Cu production increased to 40%

in the last 15 years and some products, such as brass rods, are made entirely from recycled Cu and brass [14]. It is worth noting that in the period 2000–2012, the global Cu scrap exports of the US almost doubled to reach nearly 6 million metric tons [5].

The production of secondary Cu is based on direct melt of "new scrap" (waste resulting from either metals discarded in semis fabrication or generated during the initial manufacturing process) and/or recycling of "old scrap" (obsolete end-of-life products or structures) [5]. Old scrap is often contaminated to a certain degree, depending mainly on its origin and the efficiency of collection systems [15]. Scrap metal recycling involves a number of steps such as recovery, sorting, brokering, baling, shearing, and smelting [16]. Scrap processing is accomplished through manual, mechanical and pyrometallurgical or hydrometallurgical methods. Manual and mechanical methods include mainly sorting, shredding and magnetic separation, while the scrap can then be pressed into briquettes by a hydraulic press. Pyrometallurgical pretreatment includes sweating, burning insulation from copper wire and drying in rotary kilns to volatilize oil and other organic compounds. Hydrometallurgical pretreatment includes flotation and leaching to recover copper from slag and usually produces low quality residues.

Pyrometallurgical and hydrometallurgical processes are similar to those used in primary metal production. In some cases, primary and secondary production consider the integration of secondary raw materials into common production processes to save energy and thus minimize production cost [14]. The quality of the Cu scrap defines its treatment (Figure 2). The lower grade scrap is smelted and refined like a Cu concentrate. Higher grade scrap is fire refined and subsequently electro-refined. The highest-grade scrap (mainly manufacturing waste) is often melted and cast without refining [6].

2. Zinc Production

Zinc has been identified as one of the fifty-four materials that are important to the EU's economy. China (39%), Australia (11%) and Peru (10%) are the top three largest producers of Zn, predominantly by primary mining. Europe has produced approximately 1 Mt of Zn in 2014, which is 8% of its total worldwide output. The Republic of Ireland (27%), Sweden (21%) and Turkey (20%) are the largest producers of Zn within Europe [17]. Global refined Zn consumption was around 14.5 Mt in 2015. In the developing world, Zn demand is expected to grow at an average rate of 2.2% per annum until 2035 (the annual Zn consumption is expected to increase at about 630,000 t/year) [18]. The majority of global Zn consumption growth will be in China, which is expected to increase over 50% its market share by 2020. Sixty percent of this figure will be used for galvanizing to protect steel from corrosion. Approximately 15% will be attributed to the production of Zn base alloys, mainly in the die casting industry, 14% will be used for the production of brass and bronze and 8% for the production of compounds such as zinc oxide and zinc sulfate. The remaining quantities will be used for the production of Zn alloys, mainly rolled, utilized in semi-manufactured applications including coinage and architectural applications [19]. A summary of Zn sources considered in this review as well as the main production technologies are shown in Figure SI2.

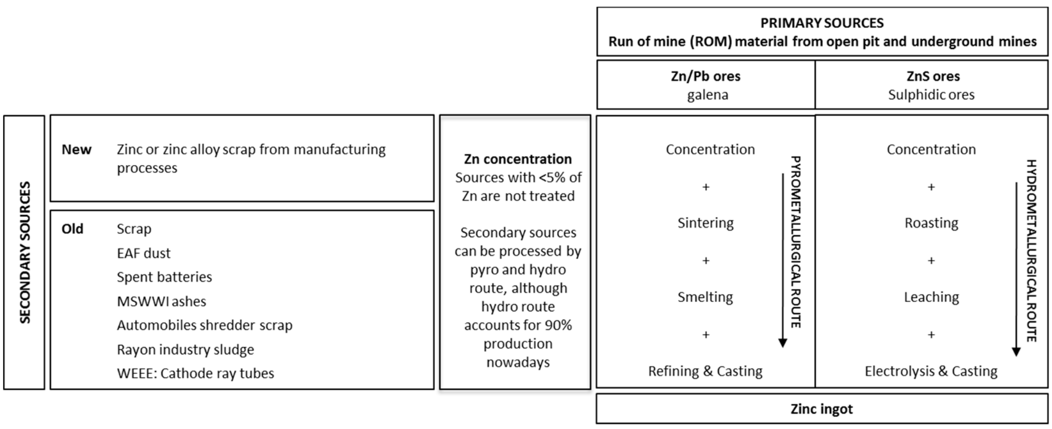

Figure SI2. Summary of Zn sources and main recovery methods. Adapted from [3,6,7].

2.1. Primary Production of Zn

Zinc is mined from underground (80%) and/or open pits [19] from Zn-Pb ores, or from other ores containing Cu, Au or Ag. The most abundant source of Zn is the mineral sphalerite, ZnS, or Zn blende. Zn is mainly recovered through pyrometallurgy or hydrometallurgy. In the case of ZnS ore, a hydrometallurgical approach is followed, where the ore is concentrated by froth flotation, roasted to convert the zinc sulfide to oxide which is then leached out with sulfuric acid to provide a leach solution that can be purified before recovering Zn by electrowinning. In the case of Zn-Pb ores, a pyrometallurgical approach is followed in blast furnaces [12,19], and the main steps involve sintering, smelting, refining and casting.

2.2. Secondary Production of Zn

Zinc can be also recovered from different secondary resources with different levels of impurities including among others ash, zinc dross, flue dusts of electric arc furnace and brass smelting, automobile shredder scrap, rayon industry sludge and cathodic tubes from WEEE. Recovery from these sources eliminates the option of disposal which today is considered expensive and environmentally unacceptable because of the increasingly stringent environmental protection regulations. Furthermore, most of these materials are classified as hazardous wastes due to their increased toxicity as a result of the presence of different metals including Pb, Cd, As and Cr. In view of the above, there has been an increasing interest in developing new processes for the recovery of Zn from these secondary sources in order both to valorize these wastes and reduce the environmental risk associated with their disposal. The processes used may produce a residue which can be recycled for further processing or safely disposed. Usually, pyrometallurgical and hydrometallurgical processes are employed for treating such secondary materials, but they are not widely used for low-concentration streams. The hydrometallurgical process, also known as the electrolysis process, or Roast-Leach-Electrowin (RLE) process, is way more used than the pyrometallurgical process. In fact, over 90% of Zn is produced today by hydrometallurgical processes [19]. Regarding the pyrometallurgical process, its main concept relies on the reduction of zinc oxide using carbon and on the distillation of the metallic Zn from the resulting mix in a carbon monoxide atmosphere. This approach of Zn recovery is very energy-intensive and has been practically abandoned in line with the rise of energy prices. A representative of this concept is the Imperial Smelting process. Today, pyrometallurgical processes account for about 10% of Zn production and are only operative in China, India, Japan and Poland.

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Conflicts of Interest: The authors declare no conflict of interest.

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