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A Review of the Risks of Copper Foil Manufacturing Plants. A New Facility in Catalonia, Spain

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Abstract

Electrolytic copper foil (elecfoil) is a thin copper foil with a thickness less than 10 μm , which is made through electrolysis of a copper sulfate solution. It is an essential component for the manufacture of electric batteries. More specifically, it is widely used to make cathode collectors in rechargeable lithium batteries. For coming years, the expected demand of elecfoil is potentially very important. Therefore, there will be an evident need of new manufacturing plants of copper foil. In relation to this, as it can happen with any industrial facility, elecfoil manufacturing plants may pose potential environmental and health risks. These risks may affect to the surrounding ecosystems, as well as to the population living in the vicinity of the facilities. Contamination of air (particulate matter, SO₂, NO_x, VOCs), water (copper and other heavy metals), and soil (heavy metals and other harmful substances) is an issue of notable concern. In Mont-roig del Camp (Catalonia, Spain), a new elecfoil is currently planned. Considering the social concern that this facility –the first one in Spain- has raised in the population of the area, the current state-of-the-art on the electrolytic copper foil manufacturing plants is here reviewed. The scientific databases Scopus, PubMed and Google Scholar, as well as information obtained from different sources (Internet) were used. The available information is very scarce, if any. Anyhow, to minimize the potential negative environmental and health impacts of new elecfoil manufacturing plants, strict periodical controls, comprehensive environmental management systems, and relevant regulations are strongly required.

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1. Introduction

Mont-roig del Camp is a town of approximately 14,000 inhabitants, which is located in the Baix Camp County, Tarragona Province (southern Catalonia). It includes two populated areas: the historic municipality in the interior, and the beach resort of Miami Platja on the coast (Mediterranean Sea). The economy of these zones is mainly focused on agricultural activities and tourism, respectively, with a very low industrial activity. Recently, the Korean multinational company Lotte Energy Materials presented a project to set up a new industrial facility in the municipal term of Mont-roig del Camp. This project is aimed at constructing a manufacturing plant -expected to be operational in 2025- with a capacity of production of **30,000 tons of elecfoil** (high-end copper foil for electric vehicle batteries) per year. This project means an initial investment of almost **400 million euros**. While most councilors of the Mont-roig del Camp City Council agree with that project, an important part of the population strongly rejects it by a number of different reasons. At first sight, anyone could think that this is a typical NIMBY (Not-In-My-Backyard) case. It is well-known that the siting of “NIMBY facilities” is often accompanied by a strong opposition of local communities, with their constructions meaning a very serious problem ^[1]. However, to better understand the opposition to the new Lottes’s facility, it is important to consider the social characteristics of Mont-roig del Camp. The town belongs to Tarragona Province, one of the four Provinces of Catalonia. In Tarragona Province, there are currently located three active nuclear power plants, having been closed a fourth one after a serious incident occurred three decades ago. In that Province is also located the largest petrochemical industrial complex of Southern Europe, which includes a big oil refinery and numerous chemical/petrochemical industries that emit various environmental pollutants. In addition, the only hazardous waste incinerator in Spain, as well as a municipal solid waste incinerator, and various landfills are also placed in Tarragona Province. The location of this entire set of facilities means that the population of this Province has a high threshold of sensitivity to any new industrial project on which they feel that might mean additional environmental and/or health risks.

From a complete ignorance of the potential adverse effects on the environment and public health that the new facility can mean, only a wide knowledge of its impact could reasonably help to reduce the current opposition among the population of the area under its influence. The pollution of air, water, and soils, as well as the human health and ecological risks are issues of concern.

The objective of the current paper has been to review and summarize the data -available in the scientific literature- directly related with electrolytic copper foil manufacturing plants, in particular, as well as those on the environmental impact and health risks of other kinds of copper facilities. The databases PubMed (<https://pubmed.ncbi.nlm.nih.gov/>), Scopus (<https://www.scopus.com/>), and Google Scholar (<https://scholar.google.com/>), as well as a general search in Internet, have been the basis to prepare this article. The terms used for the search were the following: “elecfoil”, “electrolytic copper foil”, “copper production”, “environmental copper”, “human exposure to copper”, “copper toxicity” and “ecotoxicity of copper”.

2. Copper and elecfoil manufacturing plants

The copper foil market is experiencing a considerable growing. There is currently a considerable demand from the electronics industry, considering that copper foil is an essential component in the production of printed circuit boards, as well as the increasing adoption of copper foil in electric vehicles. Regarding this, there is an important demand for high-performance lithium-ion batteries (LIBs), which rely heavily on copper foil sheets and rolls. Taking into account the significant continuous increase in the demand of copper foil for all these applications, it would not be wrong to think that, in the next years, the current trend should continue to drive growth in the market ^[2].

Electrodeposited copper foil, also known as electrolytic copper foil, or “elecfoil”, is produced by electroplating copper onto a rolling drum in a highly controlled manner. Given the properties of elecfoil, mainly the uniform thickness, as well as the excellent electrical conductivity, it is being ideal for high-performance electronic applications. Elecfoil is made by electrolysis of copper sulfate solutions, having a thickness of less than 10 μm . It is an essential material, which is used in cathode current collectors for large secondary batteries, including electric vehicles or energy storage systems, for example. As above indicated, one of the most important current uses of elecfoil is as the collector for rechargeables LIBs, where carbon paste is applied on top of the elecfoil, composing the anode of these batteries. Elecfoil can be only used with copper since any other metal flows out when it is potentially used. In addition, thinner copper foils are even required to increase the volume of rechargeable batteries. As the number of electric vehicles increases, the demand for copper foil also significantly increases in parallel. According to the International Energy Agency (IEA), the number of electric cars on the road is expected to reach 145 millions by 2030, up from just over 11 millions in 2020.

The process for the electrolysis of Cu^{2+} is here depicted (Fig. 1).

Theory diagram for the electrolysis of COPPER(II) SULFATE SOLUTION with CARBON ELECTRODES

Method of collecting electrode products ignored in this diagram
(c) doc b

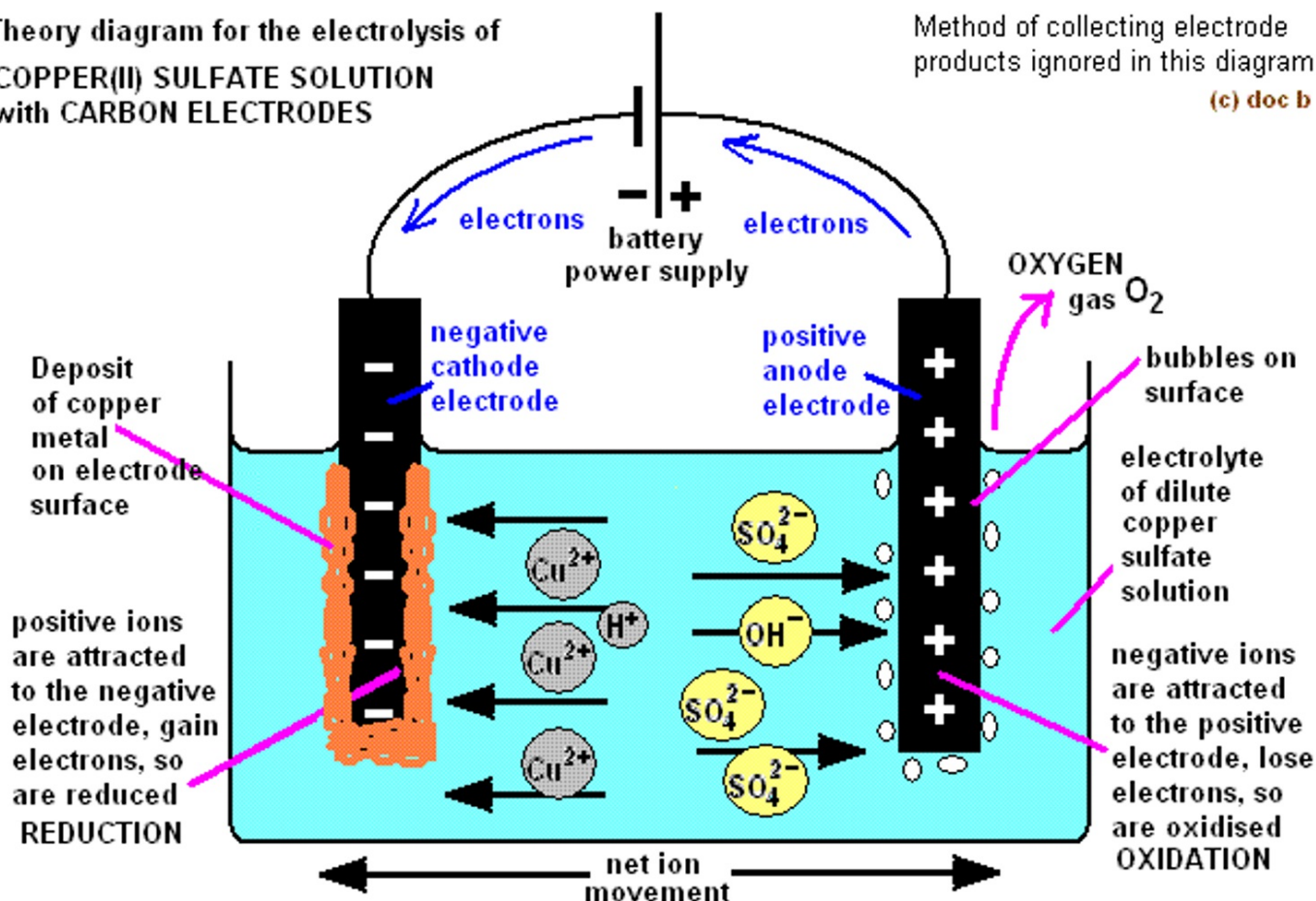


Figure 1. Diagram for the electrolysis of Cu^{2+} (Source: copied from Doc Brown's Chemistry, <https://www.docbrown.info/page01/ExIndChem/electrochemistry04.htm>).

3. Copper, environment and health

With respect to the presence of copper into the environment, it is well known that the mining and production of this metal can mean various adverse impacts [3][4][5]. These impacts include -among others- water and soils pollution, and emissions of greenhouse gases [6][7][8][9][10][11]. The potential ecotoxicological effects of copper are also another issue of concern related with the presence of environmental copper [12][13][14][15]. As a result, the copper industry is facing increasing scrutiny and pressure to reduce its environmental footprint. This can lead to regulatory challenges for copper foil manufacturers and, consequently, to limit their ability to expand production.

Regarding the health risks of copper, it is important to highlight that copper is an essential micronutrient for humans, animals, and plants. However, as it also happens with any other element or substance, its potential beneficial or adverse effects will depend on the concentrations to which the individual is exposed. For essential and/or toxic elements (including copper), it is well established that humans may be exposed to them through various pathways (inhalation, dermal and ingestion). However, for non-occupationally exposed populations, it is well established that the diet -including drinking water- is the main route of entrance of metals to the human body, accounting for more than 90-95% of total exposure [16][17][18][19]. Regarding metal contamination of vegetables and fruits, it must be noted that water irrigation is

among the major sources of soil contamination. Thus, irrigation with metal-polluted water may mean an increased soil contamination, and a subsequent metal uptake by food crops grown on such contaminated soils [20][21][22]. Excessive accumulation of metals in agricultural soils could result not only in soil pollution, but also lead to elevated metal uptake by crops, affecting food safety [22].

4. Copper production: Risks for human health

4.1. Metallurgy/smelting and e-waste

Copper production is a complex and multi-stage process that involves several stages, going from mining to smelting, refining, and finally, waste management. Since that mining copper is out of the objective of this paper, the environmental impact and the potential health effects derived from those activities have not been here included. For those interested in that specific issue, in the scientific literature there are a number of recent articles where the state-of-the-art has been assessed [3][4][5][10][23][24][25][26].

Information on the environmental contamination from copper facilities/industries, as well as the health risks to local residents is next summarized. Izydorczyk et al. [27] reviewed the environmental contamination derived from metallurgy of copper and the methods of management. Copper pollution of air, water and soils were considered, as well as the direct and indirect ways of human exposure. It was concluded that scientific data about the impact of pollutants from metallurgy on the ecosystem and on humans, were very limited. In this sense, considerable efforts should be carried out to improve the technology, control, and reduction of emissions. To conduct biomonitoring programs was also suggested by Izydorczyk et al. [27]. In China, Hu et al. [28] assessed the health risks to local residents from exposure to six (Zn, Cr, Fe, Ni, Pb and Cu) metals in samples of foods that were collected in three villages around the largest copper smelter in the country: the Guixi Smelter (Guixi City, eastern China). The health risks of the dietary intake of these metals were evaluated using the estimated daily intake (EDI), the target hazard quotient (THQ), and the Hazard Index (HI). Samples of hair and urine of local residents were collected and analyzed for the content of the examined metals. The THQ of each individual element and the HI of combined elements showed that the EDI of lead and copper had the highest potential health risks. It was also found that the levels of the analyzed metals -including copper- in hair and urine were much higher than those found on Chinese individuals living in areas out of the influence of the copper smelter. Also in China, Yang et al. [29] carried out a study on life cycle assessment (LCA) and cost analysis for the copper hydrometallurgy industry. It was concluded that leaching had environmental advantages to extract low-grade copper ore, but regardless of which leaching route, the decreasing ore grade would enlarge environmental impacts, mainly a great consumption of electricity, as well as sulfuric acid.

Recycling electronic waste (e-waste) is another potential source of environmental copper. Human exposure to metals from recycling e-waste -as occurs with any emission of environmental pollutants- occurs through inhalation, intake (mainly food and drinking water) and dermal absorption. Kang et al. [30] studied the environmental impact and the potential human health effects of rechargeable lithium batteries in e-waste. Among the analyzed metals, it was found that cobalt, copper,

and nickel were the main contributors to the total hazard potential. Interestingly, for all the used methods in that study, copper had a mostly large to medium relative contribution to the total hazard. The minimal contribution of copper for human toxicity corresponded to emission to water based on CML (Centre of Environmental Science Method). Copper was also among the metals most associated with potential human toxicity and ecotoxicity. On the other hand, Zeng et al. [31] reviewed the adverse effects of various metals (including copper) on children living near an e-waste recycling area in Guiyu, China. It was found that the analyzed metals -either individually or under multiple combinations- influenced various organs and systems, which would result in acute and chronic adverse health effects on children. In turn, Wu et al. [32] measured the levels of ten metals (being copper one of them) in particulate matter (PM) in an e-waste dismantling park and its neighboring areas in Guiyu, Guangdong province, China. Health risks for the population living in the vicinity were also assessed. The levels of metals in PM were compared with national and international guidelines/standards. Lead, Ni, Fe, Mn, Zn, Cu, and Cd were detected in the e-waste site. Considering that there is no standardization or guidelines for Cr, Zn, Cu and Fe in atmospheric PM, the metal pollution found in that survey might be even more severe within the dismantling and residential areas. To investigate the potential exposure biomarkers of e-waste, Kuang et al. [33] examined the differences in exposure levels to various volatile organic compounds (VOCs) and metals/metalloids in children living near an e-waste recycling area (ER) and a non-ER in Guiyu town, China. Compared with children of the non-ER, those living near the ER were -in general- exposed to higher concentrations of metals, and also higher levels of VOCs. In ER children, the urinary levels of various metals -including copper- were between 1.2 and 2.4 times higher.

Nfor et al. [34] measured the levels of various metals in soils from e-waste activity sites in Douala, Cameroon. The effects of these metals in soils on the growth and reproduction of a local earthworm species, *A. nilotica*, were subsequently assessed. E-waste had a different soil metal profile (Cu > Pb > Zn > Cr > Ni > Co > As > Cd > Hg) from that of the non-e-waste soils, being growth and reproduction of *A. nilotica* significantly inhibited when exposed to e-waste soils. On the other hand, in China Zhang et al. [35] used the life cycle assessment (LCA) method to analyze the global environmental impact of copper-based mixed waste recovery. To evaluate the differences in the environmental impact associated with recycling processes, the results were compared with those obtained for primary copper production. It was found that, on average, in China the environmental impact of the copper-based mixed waste recovery process was generally higher to that of primary copper production. Nevertheless, it would be lower to that of secondary copper production.

4.2. Lithium-ion batteries (LIBs)

Although most studies on the environmental impacts of copper production have mainly focused on primary copper metallurgy/smelting, recycling, and other processes, the life cycle assessment (LCA) method has been also used to analyze the environmental impact of the stacking of copper tailings. An interesting case is that of the lithium-ion batteries (LIBs). Due to their high energy density and long cycle life, LIBs have been and are being widely used in communication, electronics, transportation, as well as in other fields, which play an important role in our advanced societies [36][37][38][39]. Lithium-ion batteries are currently among the most used in electric passenger cars [38], being the anode current collector of these batteries mainly electrolytic copper foil. In relation to this, it has been reported that reducing the roughness of electrolytic copper foil might be a feasible route to improve the performance of LIBs [35].

Arvidsson et al. [40] quantified the life-cycle health impacts of a cobalt-containing lithium-ion battery. These authors reported that emissions from production of nickel sulfate -which is used in the cathode- and that of copper foil -which is the anode current collector- contributed with 30% and 20%, respectively, to the total life-cycle health impacts of the LIB cell. Regarding specifically to the potential health impacts of the copper foil production, these were the following: human non-carcinogenic toxicity (68%) and fine particulate matter formation (19%). For PM formation, the main contribution comes from the mining of platinum group metals, from which copper is a byproduct, basically due to SO₂ emissions. One of the recommendations of Arvidsson et al. [40] was to assess the feasibility of replacing the copper foil with another material, which can provide anode current collector functionality. In turn, Mrozik et al. [37] have reviewed the environmental impacts, as well as pollution sources and pathways of spent LIBs. These authors reported that the toxicity of the LIBs material could mean a direct threat to organisms on various trophic levels. It might also be a direct threat to human health. Mrozik et al. [37] identified potential contamination pathways, which would be leaching, disintegration and degradation of the LIBs. In relation to copper in leachates, it was found to exceed toxicity limits (together also with those of lead, mercury, cobalt, nickel, chromium, and thallium).

On the other hand, Yang et al. [39] conducted a study aimed at preparing ultra-thin copper foil as current collector to improve the performance of LIBs. Reduced carbon footprint was used. Copper resource savings and carbon footprint reduction were confirmed by adopting ultra-thin copper foils. From a perspective of resource savings, the authors estimated that -in 2030- 4.5 µm lithium battery copper foil could save 32 million tons of copper metal in comparison with 9 µm copper foil. Moreover, with respect to environmental protection, it was suggested that 40.6% of the carbon emissions might be eliminated by reducing the thickness of copper foil (from 9 µm to 4.5 µm). Recently, Gutsch and Leker [41] examined the costs, carbon footprint and environmental impacts of LIBs, going from cathode material synthesis to cell manufacturing, and finally recycling. It was reported that, for cell manufacturing, nickel, cobalt, and copper accounted for >83% of combined environmental impacts. Consequently, high recovery rates for these elements should ensure that much recycled materials might replace raw materials. Recently, Shahraki et al. [12] published an interesting review, which was focused on two main objectives: a) the environmental evaluation of copper cathode production -at midpoint and endpoint levels- and b) the assessment of its contribution to emissions of greenhouse gases (GHG). The study was based on life cycle assessment (LCA). The most relevant results were that the applied chemicals in the copper cathode production significantly increased freshwater and marine ecotoxicity, as well as human toxicity, which would be the result from heavy metal leaching from the smelting stage. Moreover, the release of CO₂ from fossil fuel burning during the copper cathode process was also a key issue from the global warming.

5. Copper toxicity in humans

Since many years ago, it is well established that copper plays an essential role not only for humans [42][43], but also for animal and plants [44][45]. Copper is necessary for various basic body functions, which include from forming enzymes that produce energy or balancing hormones that make nerve cells, to regulate gene expression and to promote healthy immune system functioning, among other important essential functions. However, although in individuals who are non-

occupationally exposed to copper, toxicity of this trace element is rather rare, exposure to high levels of copper from contaminated air, water and food, can cause adverse effects in humans. An excess or toxicity of copper has been associated with hepatic disorders, neurodegenerative changes, as well as other diseases, which may occur when the homeostasis of copper is disrupted [46][47][48][49]. One of the most known human disorders related with copper is Wilson's disease. This serious disease is an inherited disorder of copper balance, which leads to hepatic damage and neurological disturbances [50][51]. Even in recent years, some studies have identified some metal (basically iron, copper and zinc) dyshomeostasis as a potential neurotoxic factor of Alzheimer's disease (AD). Notwithstanding, the links between these essential metal ions and the risks of AD are rather ambiguous [52]. Anyhow, among the metals that could be involved in the pathogenesis of AD, copper ions would seem to be central in the formation of plaque and soluble oligomers, and therefore, could have an essential role in the AD pathology [53][54][55]. In summary, although according to the extensive scientific literature on the effects of copper on human health, its essentiality seems to be -in principle- more worrying than its potential toxicity, under some circumstances this cannot be underestimated at all. A very complete and excellent report on the toxicological profile of copper was recently published by the Agency for Toxic Substances and Disease Registry (ATSDR) [56]. In turn, the European Food Safety Authority (EFSA), by means of its Scientific Committee (SC), has also published a recent review [57] that was prepared with the following two aims: a) to provide a scientific opinion on an acceptable daily intake (ADI) for copper, and b) to perform a new estimation of copper intake, considering all human exposure sources. The SC of the EFSA concluded that copper should not be retained in the body with an intake of 5 mg/day, whereas an ADI of 0.07 mg/kg body weight was established. In its report, the SC highlighted that background copper levels are a significant copper source [57].

6. Discussion and conclusions

Despite the extensive search carried out in the scientific literature to prepare the current paper, not a single article, in which the assessment of environmental or human health risks derived from the activity of electrolytic copper foil manufacturing plants, is currently available in the databases PubMed, Scopus and Google Scholar. Does it mean that these plants are so safe that they do not need to be subject to periodic controls and evaluations? If studies have been carried out, why the results have not been published in scientific journals?

In the 20th and 21st centuries, there has been in the world various serious environmental man-made disasters that have been due to human or technical errors in the functioning of industrial facilities (or even in their plannings) of various types. However, all of them had a common denominator: they had been considered "safe". These are just a few examples: the Seveso disaster, the Chernobyl meltdown, the Bhopal disaster, or the more recent Fukushima nuclear accident. Obviously, and without acquiring this tremendous relevance, the number of annual incidents in industrial activities is considerable. The number of affected persons by "minor" incidents/accidents is comparatively with the big disasters, certainly much lower. However, this does not mean that the environment and/or public health result -more or less- impacted by acute or chronic emissions of a number of pollutants. Logically, when a new industrial activity is authorized in a certain place, all the international/national/local requirements are set. Nevertheless, over time and due to different

reasons, such as accidents/incidents, malfunction, or lack of rigorous controls, the environmental and/or health risks near the facilities can become relevant. Therefore, periodical controls of the facilities/industries, as frequent as possible, are strongly recommended. In the current case, for the planned facility, these air pollutants should be monitored: PM₁₀, PM_{2.5}, SO₂, NO₂, and VOCs, as well as the content of heavy metals in PMs. The concentrations of metals, with very special emphasis in copper, should be also measured in water and soils samples collected near the new facility. Also, the levels of various heavy metals in vegetables and fruits grown in the area under potential influence of the plant should be measured [58]. Anyway, according to our long experience in risk assessment, in order to estimate the carcinogenic and non-carcinogenic risks for the population living near industrial facilities, which may entail some kind of risk, specific studies might be required [59][60]. Thus, health studies should consider the potential interactions among chemicals, while epidemiological investigations that can guarantee the absence of adverse effects could be also necessary.

Anyway, the most important conclusion of the current review is that there is not information -available on scientific journals- about the characterization and evaluation/assessment of the environmental and health risks of this kind of facilities.

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