DESAFIOS AMBIENTAIS E SOLUÇÕES TÉCNICAS NA ADAPTAÇÃO DA INDÚSTRIA DO COBRE AOS CRITÉRIOS ESG*

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Resumo

A produção de cobre de alta pureza está se tornando cada vez mais difícil, pois a pureza dos minérios diminui gradualmente após várias décadas de mineração intensiva. Para reduzir o efeito danoso das impurezas, presentes nos minérios, foram adicionados processos de purificação do eletrólito no processo de eletrorrefino. No entanto, essa prática resulta na perda de metais valiosos como antimônio (Sb) e ácidos (HCl), o que não está associado a uma ideia de economia circular, onde os resíduos ocorridos na fase de produção possam ser reciclados e, portanto, se tornar um recurso. Além disso, o Sb é listado como uma matéria-prima crítica nos EUA e na UE, sendo um material considerado de disponibilidade limitada, tanto pela pegada ambiental de seu fornecimento quanto pela pressão geopolítica e social por alguns minérios e elementos. Assim, tecnologias para reciclar Sb e ácidos de efluentes gerados durante a produção de cobre devem ser avaliadas. Este trabalho aborda o desafio de aplicar técnicas eletroquímicas e processos de separação por membranas no processamento de minerais sulfetados de cobre, não apenas para purificação do eletrólito (HCl), mas também para recuperação de Sb. A conquista do reaproveitamento e reciclagem de matérias-primas em uma economia circular é importante, pois a metalurgia do cobre deve ser sustentável, equilibrando lucro, segurança, aceitação social e proteção ambiental. Os resultados demonstraram que é possível obter Sb metálico usando o processo de eletrorecuperação e, ao adicionar uma membrana catiônica no sistema, a recuperação de Sb metálico foi superior a 90% devido à melhora das condições hidrodinâmicas de transporte e da ausência de reações de oxirredução que ocorrem sem a membrana. Além disso, foi possível recuperar o eletrólito por processo de diálise reversa.

Palavras-chave: Efluente da mineração do cobre; processos eletroquímicos baseados em membrana; recuperação de Sb e eletrólitos; economia circular.

ENVIRONMENTAL CHALLENGES AND TECHNICAL SOLUTIONS IN ADAPTING THE COPPER INDUSTRY TO ESG CRITERIA

Abstract

The high purity copper production is becoming increasingly difficult as the purity of mineral ores gradually decreases after several decades of intensive mining. To reduce the damaging effect of the impurities, present in mineral ores, processes have been added to purify the electrolyte on the electrorefining process. Nevertheless, this practice results in the loss of valuable metals as antimony (Sb) and acids, what is not associated to a circular economy idea, where waste occurring during the production phase could be recycled and, therefore, become a resource. Moreover, Sb is listed as a critical raw material in the US and in the EU, being a material considered as one with limited availability, both because of the environmental footprint of its supply and

because of the geopolitical and social pressure for some ores and elements. Thus, technologies to recycle Sb and acids from the wastewater generated during the copper production must be evaluated. This work addresses the challenging subject of applying an electrochemical technics and membrane process in the processing of copper sulphide minerals, not only to purify the electrolytes (HCl), but also to recover Sb. The achievement of reuse and recycling of raw materials in a circular economy is important, since the copper metallurgy must be sustainable, balancing profit, safety, social acceptance and environmental protection. The results demonstrated that it is possible to obtain metallic Sb using the electrowinning process and, when adding a cationic membrane in the system, the recovery of metallic Sb was greater than 90% due to the improvement of the hydrodynamic conditions of transport and the absence of redox reactions that occur without the membrane. In addition, it was possible to recover the electrolyte by reverse dialysis.
Keywords: Cooper wastewater; electrochemical membrane processes; Sb and electrolyte recovery; circular economy.

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1 INTRODUCTION

The ESG (environmental, social and governance) criteria were discussed for the first time in 2004, in a joint initiative of 20 financial institutions, which were invited by the UN to develop guidelines and recommendations for the integration of social, environmental and governance criteria to the capital market. This initiative resulted in the publication of the *Who Cares Wins* document. In this document, the financial institutions state that companies, which in their management consider environmental, social and sustainable governance criteria, are more competitive and present a lower financing risk, since they are capable of properly managing operating risks, anticipating regulatory action, or access to new markets, in addition to contributing to the sustainable development of the regions where they operate [1].

The mineral extraction sector is of great importance for the South American economy. With increased awareness among investors and community groups, responsible mining needs to be linked to ESG issues, with companies now being required to incorporate ESG principles into their operations. In fact, the companies must show good environmental and social operations [2], and these operation aspects must be presented in the form of indicators [3].

Different environmental sustainability indicators are considered on the literature to mining and processing of copper [3]. One environmental issue is related to the generation of wastes containing critical minerals. Every year, copper mining is related to lower grade sources, generating increased amounts of wastes to be disposed of [2]. By applying ESG principles, one environmental sustainability indicator could be the critical raw materials recycling rate. This may incorporate circular economy concepts on the ESG principles of the copper processing industry.

Critical raw materials are those with limited availability, both due to the environmental footprint of their supply and the geopolitical and social pressure for some ores and elements. Antimony is considered a Critical Raw Material both in EU [4] and USA [5]. On the other hand, China has the largest reserves of Sb in the world, dominating also Sb mining (± 78% of global production capacity) [6].

Antimony is an impurity on copper refining electrolyte. The difficulties caused by the presence of metal impurities in copper metallurgy have already been described in the literature [7-9]. To reduce the damaging effect of these impurities, during the manufacture of copper, processes have been added to purify the electrolyte on the electrorefining process [8, 10]. The most common practice is the use of ion exchange resins, specially designed to antimony and bismuth removal from the copper electrolyte. By the ion-exchange regeneration, the loss of valuable metals as antimony will happen, what is not associated to a circular economy vision, where “waste occurring during the production phase could be recycled and therefore become a resource”.

Copper mining and processing are associated with large water consumption and effluent generation. But these processes must be sustainable, balancing profit, safety, social acceptance and environmental protection. Thus, new effluent treatment processes must be encouraged to minimize risks to water security. This work addressed the challenging subject of applying electrochemical processes (electrowinning and membrane electrolysis) in the treatment of the wastewater generated by the ion-exchange regeneration, not only to purify the electrolytes, but also to recover Sb. The studies were carried out with the objective of achieving a copper production with less environmental impact, minimizing the generation of effluents and wastes and maximizing the metals recovery.

2 WORK DEVELOPMENT

Copper is usually extracted by means of two different procedures, depending on the origin of the ores: the hydrometallurgical method is employed with copper oxide and mixed minerals, while the pyrometallurgical method is used with copper sulfide ores [11], as shown in Fig. 1. In the hydrometallurgical process, leaching of the ores with H_2SO_4 is followed by solvent extraction; where a solution concentrated in copper is finally obtained for the electrowinning process. On the other hand, in the pyrometallurgical process, grinding and milling of copper minerals is followed by subsequent steps of flotation, filtering and smelting. After extraction of the metal, in both processes, an electrorefining step is conducted to achieve copper with high purity. In some copper industries, the spent electrorefining electrolyte is passed through ion exchange beds to separate the metallic impurities and recycle the sulfuric acid employed in the electrorefining. In those industries, after a given number of cycles, the ion exchange system is regenerated with hydrochloric acid (HCl) and, as a result, a highly concentrated HCl solution containing mainly Sb and Bi, is obtained. Presently, this wastewater is discharged without recovering the HCL and the valuable metals like Sb and Bi [12].

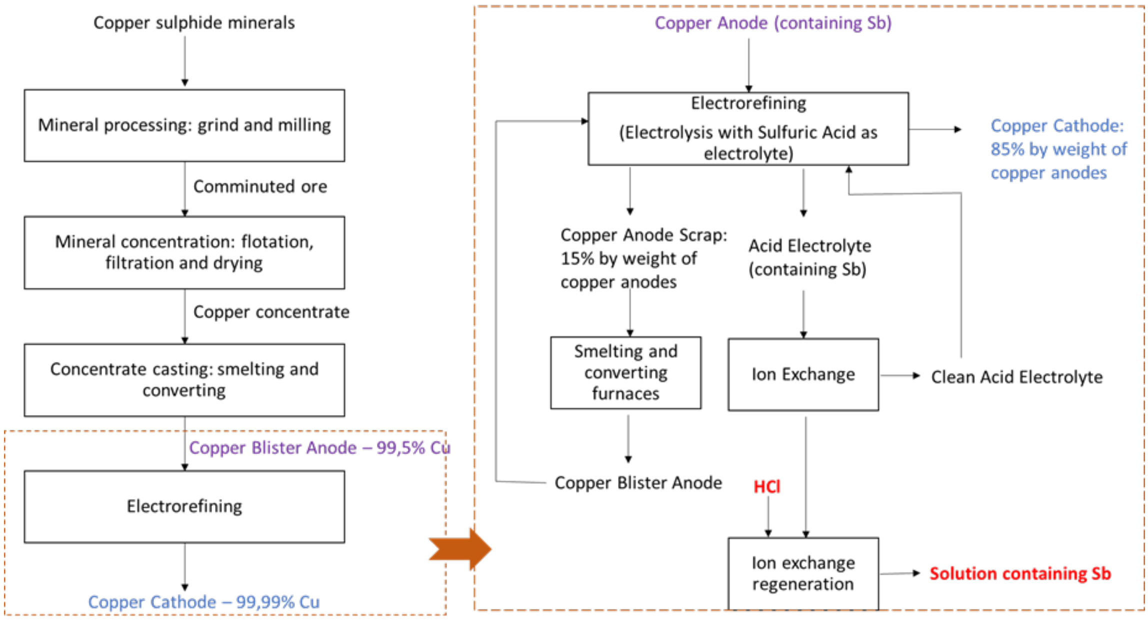

Fig. 1. Copper production from copper sulphide minerals by pyrometallurgical process.

To implement the principles of circular economy in the copper production, Sb losses should be avoided and the recovered HCl solution should be further reused in the regeneration of ion exchange resins, thus ensuring a minimal release of wastewater. As shown in the last steps of the scheme of Fig. 1, in this work, electrochemical technics were proposed to treat the wastewater containing Sb to separate the metallic Sb from HCl, and also the use of direct dialysis to reconditioning the HCl to the system was evaluated.

Among the available techniques that could be used to separate Sb from waste effluents, electrowinning (EW) stands out on account of its high selectivity. This technique enables the individual recovery of a specific element present in a mixture based on the different reduction potentials of each metal. Considering that the solution obtained from the regeneration of the ion exchange resins contains a high concentration of HCl and lower concentration of Sb, and taking into account that redox reaction can occur and limited the mass transport or produce detachments of the Sb film from the cathode, membrane techniques should be employed in the electrochemical processes.

The electrodialysis (ED) is a membrane separation process in which ions are transported through ion selective membranes from one solution to another under the influence of an electric field. As a result, two new solutions are obtained: one that is more diluted and another that is more concentrated than the original one [13]. It is why ED has been widely applied in processes such as the removal of heavy metals in electroplating wastewater treatment [14]. In mining processes, ED has been tested with satisfactory results in the recovery of acid mine drainage [15] and in the treatment of copper smelter wastewater [16] among others. When the objective of the selective transport of species is to promote specific chemical reactions at the electrodes, while retaining some ionic species from others, it is called reactive electrodialysis or electro-electrodialysis (EED).

Depending on the type of membrane used, the diffusion dialysis (DD) process is based on co-ion rejection or electrical neutrality [17], that is, when anion exchange membranes are used, for example, only the stoichiometric flow of anions are admitted, while cations are rejected. In view of the possibility of coupling, H^+ protons will also pass through the system, reconditioning the acid in the diluted compartment. By reducing the concentration of HCl in the concentrated compartment, the EED process will be also facilitated, since there is a lower HCl:Sb proportionality, reducing competitiveness in transport through the membrane, in this case cationic, facilitating the recovery of metallic Sb.

2.1 Tests using a lab-scale system

In the first step, lab-scale experiments were carried out with solutions prepared to surrogate the wastewater generated at the ion-exchange regeneration step. The solution was prepared by dissolving 1g of Sb_2O_3 in 1L of HCl 6M.

Three different process and cells were used: a one-compartment cell, to the electrowinning experiments (EW), and a two-compartments cells, to the electro-electrodialysis (EED) and direct dialysis (DD) trials, where a cation-exchange and an anion-exchange membrane were applied, respectively. In the EED case, H_2SO_4 3M solution was used on the anolyte compartment, whereas in DD system deionized water was used in the diluted compartment. Fig. 2 presents the three cells used.

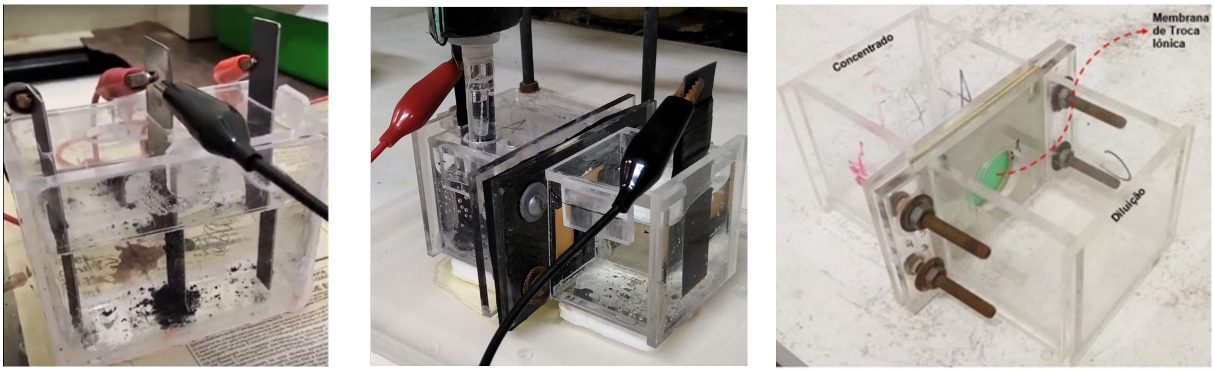

Fig. 2. Lab-scale cells (a) for EW, (b) for EED and (c) for DD. The firsts two were used to Sb-Recovery and the third to HCL recovery.

A set of tests were conducted using the EW system in potentiostatic and galvanostatic mode aiming the Sb-recovery. Results demonstrate that, the progress of the secondary electrode reactions of hydrogen and chlorine evolution causes the detachment and redissolution of the deposited Sb, in both potentiostatic or galvanostatic mode [18]. Aiming to improve the Sb recovery, since Sb concentration is low in the wastewater generated at the ion-exchange regeneration step, a cation-exchange membrane was used in the EED system, because the membrane can avoid the reoxidation of Sb(III) to SB(V) on the anode of the electrowinning cell, increasing the Sb-recovery. Other important parameter on EED process which can increase the Sb-recovery is the mass transfer. For clarify that, a series of linear sweep voltammetry were conducted using a Pt rotation disc electrode (RDE) at a scan rate of 10 $mV{\cdot}s^{-1}$ and rotation rates ranging from 500 to 4500 rpm. It is observed in Fig 3. between -0.4 and -0.5 V × Ag/AgCl, a plateau corresponding to the limiting current density, indicating that the Sb(III) reduction is under complete mass-transport control, meaning that the hydrodynamic conditions of the process have a great effect on the electrowinning rate.

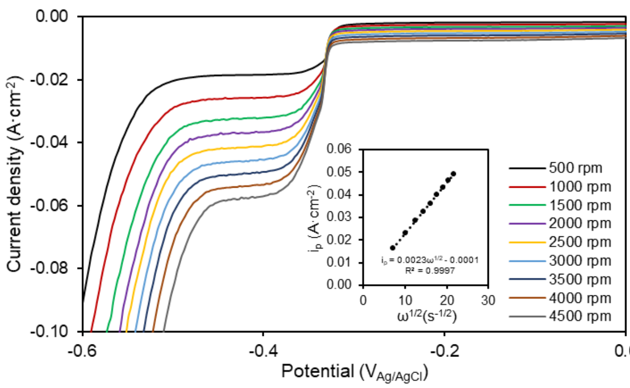

Fig. 3. Linear sweep voltammetry obtained with 1g of Sb_2O_3 in 1L of HCl 6M solution. Inset graphic: Relationship between the limiting current density and the square root of the rotation speed.

Based on these findings, EED experiments (**Fig. 2.a**) were carried out and a higher Sb recovery was obtained by the experiments carried out under magnetic stirring (**Fig. 4**) without detaching.

Fig. 4. Photo of the cathode employed in the EED lab-scale tests showing a up 90% Sb-Recovery.

The tests using the DD system aiming to HCl-recondition showed a linear increase of Cl^- in the diluted compartment (**Fig 5.a**), which agrees with the Fick's second law, where the transport flux of a given species should gradually decrease over time, as a result of the reduction in the concentration gradient. Nevertheless, the acid reconditioning capacity achieved by the system led to the removal of only 2.62% of Cl^-present in the concentrate compartment, indicating that the amplitude of concentration between concentrated and diluted solutions are still very discrepant (**Fig 5.b**). It means that the DD process could proceed for longer times.

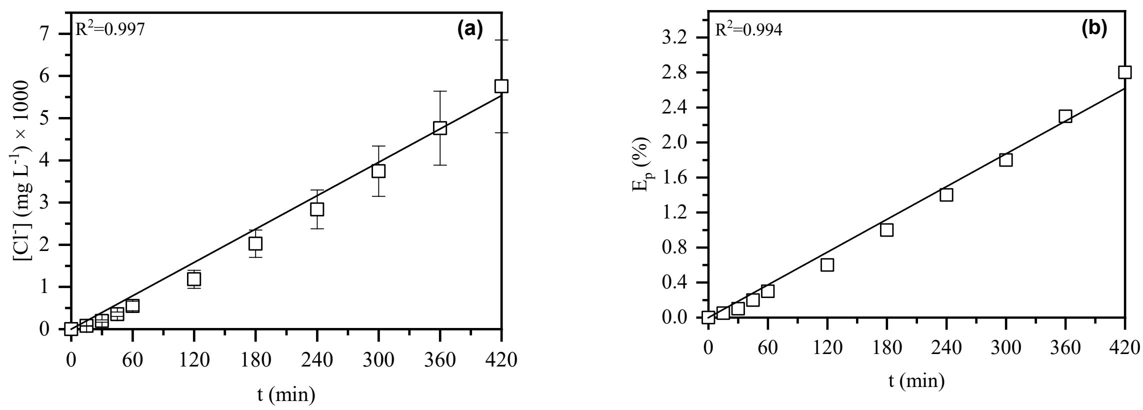

Fig. 5. (a) chloride ions concentration in the diluted compartment and (b) percentual extraction (E_p, %) of the chloride ions from the concentrate compartment.

Fig. 6.a illustrate the Cl^- transport through the membrane which are related to the sorption and diffusion phenomena [19]. The acid is first sorbed into the membrane, diffused through the material due to the driving force of concentration (coupling effects, dragging H^+), and then desorbed into the dilution compartment on the opposite side. However, it was also noticed the presence of Sb in the diluted compartment, fact that can be attributed to the $SbCl_4^-$ formation, allowing the Sb transport though the membrane (Fig. 6.b), meaning that more selective membranes need to be employed in the DD process to avoid the Sb scape.

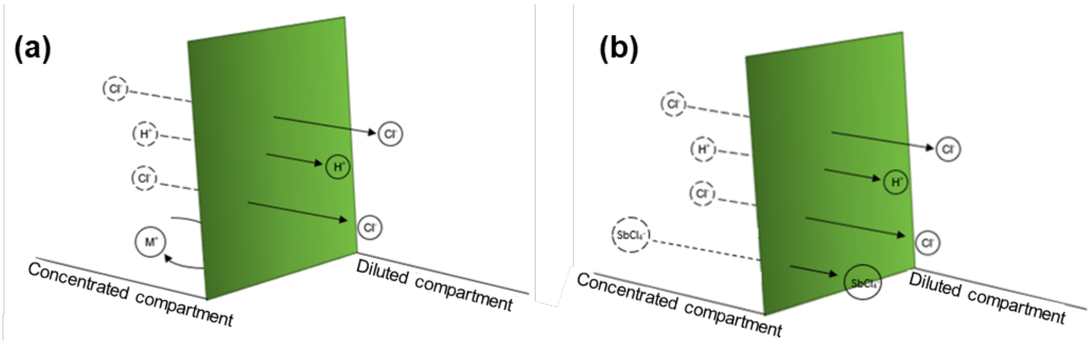

Fig. 6. (a) chloride ions concentration in the diluted compartment and (b) percentual extraction (E_p, %) of the chloride ions from the concentrate compartment.

2.3 Tests using an industrial-scale plant

Tests of EED using a DOM-TEC® industrial plant were also carried out. The plant consists in a rack with 20 cells, each with its respective stainless-steel cathode, titanium anode and ionic membrane, connected to a 100 V, 1,000 A rectifier, all inside of a container Fig. 7 [20].

Fig. 7. DOM-TEC® 40 feet container plant and its hardware.

The best result parameters obtained in several test was faradic efficiency of 92.91%, a current density of 500 A m^{-2}, cell voltage 2.3 V and rate flow solution of 600 L min^{-1}. Fig. 8 show the cathode with a 96.04% Sb and 3.7% Bi recovered from the ionic exchange (IX) eluate effluent that had an initial Sb and Bi concentration of 15 and 4 g L^{-1} respectively, in 120 g L^{-1} of HCl.

The results show that it is possible to treat copper electrolytes with different types and concentrations of impurities. It is achievable metallic Sb and Bi electrowining, and also HCl reconditioning to the system, making the process more sustainable.

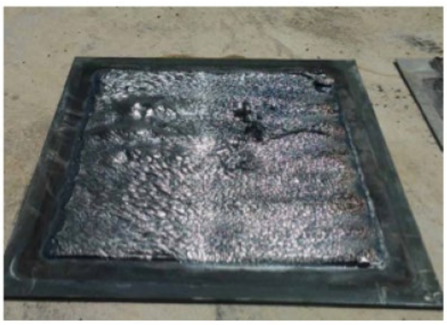

Fig. 8. Sb-Bi cathode obtained by DOM-TEC®.

3 CONCLUSION

Based on the obtained results, it is possible to conclude that the electro-electrodialysis (EED) is a process that may be applied with success to the Sb-recovery from the wastewater generated at the copper electrolyte purification, whereas the direct dialysis (DD) process can be used to reconditioning the HCl. Further developments in the subject of Sb and HCl recycling will be possible, including the treatment of other Sb containing wastes and effluents, like the ones generated by copper and lead secondary smelters, as dusts and slags from scraps processing. Considering that a recycling of waste is envisaged and that less wastewater generation is expected by the introduction of EED and DD on the copper processing route, this work addresses environmental/societal benefits.

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