EVALUATION OF THE TECHNICAL VIABILITY OF POSSIBLE APPLICATION ROUTES OF COPPER SLAG

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Abstract: This paper aims to evaluate the reuse of copper slag through hydrometallurgical and pyrometallurgical routes to recover metals contained in the waste of smelters or use it as a source of raw material in other products with higher added value. For this, waste characterization analysis were carried out using X-ray diffraction - EDS, atomic spectrometer and scanning electron microscopy – SEM. The results of flotation and leaching tests on a laboratory scale, tests using a pilot furnace with submerged lance, as well as tests in an industrial electric furnace were also evaluated. The results showed that there is technical feasibility for recovering copper, as well as a high potential for applications in the production of ceramics and porcelain tiles, beyond the uses already recognized by the market.

Keywords: Copper Slag; Waste Reuse; Economic and Environmental Sustainability; Copper Smelters; Product with added value.

AVALIAÇÃO DA VIABILIDADE TÉCNICA DE POSSÍVEIS ROTAS DE APLICAÇÕES DA ESCÓRIA DE COBRE

Resumo: Este trabalho tem como objetivo estudar o reaproveitamento da escória de cobre através de rotas hidrometalúrgicas, pirometalúrgicas ou a união destas rotas para recuperar metais contido no rejeito dos Smelters ou utilizá-la como fonte de matéria prima em outros produtos com maior valor agregado. Para isto, foram realizados análises de caracterização do resíduo utilizando difração de raio-x, espectrômetro atômico, moinho de bolas e microscópio eletrônico de varredura para realizar a caracterização do material. Os testes em laboratório de flotação e lixiviação e em escalas piloto e industriais utilizando forno com lança submersa e forno elétrico também foram avaliados. Os resultados mostraram haver viabilidade técnica para recuperação do cobre e elevado potencial para aplicações na produção de cerâmica e porcelanatos, além das outros usos já reconhecidas pelo mercado.

Palavras-chave: Escória de cobre; Reaproveitamento de resíduos; Sustentabilidade econômica e ambiental; Smeters de cobre, Produtos com maior valor agregado.

1. INTRODUCTION

A large amount of waste is produced by several copper metallurgy plants every year, resulting in the need to find alternatives to dispose of a huge variety of waste. Among the principles of the *Politica Nacional de Resíduos Sólidos do Brasil -PNRS* (Law n◦ 12.305/2010) is shared responsibility to minimize the volume of waste and rejects generated and reduce the effects caused [1]. The reuse and recycling of solid waste, included in the objectives of this policy, are alternatives that can reduce the volumes generated, the impacts on the environment and increase the added value of the by-product.

One such waste is the slag that is produced in electric copper smelter furnaces. During matte smelting, two separate liquid phases are produced: copper-rich sulfides and low-copper oxides, referred to as slag. In general, the slag from the Flash and Converter furnaces with approximately 1.5 and 5% copper content respectively are directed to the electric furnace to recover the copper contained in this by-product.

It is estimated that for every ton of copper production, about 2 tons of slag are generated. The copper content in slag is approximately 1% and the use or recovery of the metal depends on the type of slag. The current options for managing this waste are recycling, metal recovery, production of materials with higher added value and disposal in deposits or landfills [2].

In this sense, slag is produced in Copper Metallurgy understood as by-products and several studies are being incorporated with the objective of verifying the characteristics and properties aiming at the use and use in the manufacture of new products.

Another important point regarding risk management and the development of competitive advantages is carbon pricing. Pricing can take the form of carbon taxes or emissions trading schemes [3]. The use of copper slag as an alternative source of raw material for products with greater added value or recovery of the contained metals aims to avoid construction of industrial landfills, increase resource efficiency, conserve increasingly reduced natural minerals, facilitate industrial symbiosis and reduce CO2 emissions.

Therefore, analysis were carried out to characterize the slag produced in copper smelters and hydrometallurgical and pyrometallurgical tests were evaluated to reuse the waste as a source of raw material in other products with higher added value.

2. METHODOLOGY

The copper slag, also known as iron silicate, was provided by the Paranapanema Group, unit in Bahia - Brazil.

Several analyses were carried out in different institutions on the samples of granulated slag supplied by Paranapanema, the most important of which were:: Chemical composition, Granulometry, Work index and Scanning electron microscopy.

The analysis of the chemical composition of the slag was carried out using the ICP-OES atomic spectrometers of the Perkin Elmer OPTIMA 8300 and Agilent SVDV

5900 models and x-ray diffraction with the Rigaku model – Supermin 200. As a complementary methodology, a qualitative analysis was carried out via X-ray diffractometry with granulated slag (at 325# or 37mm).

To carry out the granulometric distribution, sieves of 7, 10, 24, 35, 65 and 200 mesh were used and later check the percentage retained in each sieve. The stack of sieves was placed on the RoTap and sieved dry for 15 minutes.

The Work Index (WI) is the parameter that expresses the resistance that the material offers to grinding, numerically defined as the energy in kilowatt hours required to comminute a ton of material, from a block of theoretically infinite size to the granulometric distribution in which 80% passes through a 100 micron (μm) mesh.

A sample of numerous slag granules (-6+8#) and another with powdered whole sample were mounted and polished for SEM/EDS analysis. Imaging and EDS were conducted on a TESCAN Mira3 field emission SEM using an EDAX Octane Elect EDS detector.

3. RESULTS AND DISCUSSION

3.1 Analysis of copper slag

To determine the most viable method for generating metals from a compound, it is recommended to perform mineralogical analysis to determine whether the ore has characteristics of oxides, sulphides, carbonates, etc. The result of the typical chemical composition of table 1 contains oxides such as Al2O3, CaO, MgO that are present in the original concentrate and mainly SiO2 that, in addition to being present in the concentrate, is intentionally added to improve the fluidity of the produced slag.

Table 1: Chemical composition of copper slag

Element	**FeO**	**Al_2O_3**	**CaO**	**MgO**	**Cu**	**S**	**SiO_2**
(%)	46.15	2.83	1.7	1.23	1.19	0.71	32.7
Element	**As**	**Mo**	**Na**	**P**	**Pb**	**Ti**	**K**
(%)	0.099	0.165	0.042	0.061	0.71	0.206	0.81

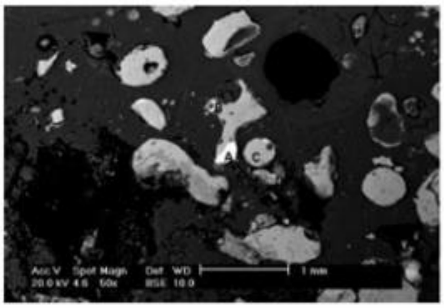
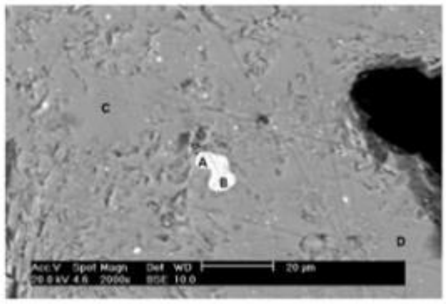
As this is a granular material, size distribution analysis were carried out and typical results indicate that the material is composed of more than 80% of grains greater than 710 mm (24 mesh), the data are shown in Table 2.

Table 2: Copper slag granulometry

MESH-POL	**7**	**10**	**24**	**35**	**65**	**200**	**<200**
mm	**2,8**	**1,68**	**0,71**	**0,424**	**0,21**	**0,07**	**<0,070**
withheld (%)	17,7	26,8	44,4	7,0	2,4	0,7	0,3

A wide-field image is shown in figure 1. Where it is possible to observe fields with high copper contents in the form of sulfides and other fields with low copper contents.

Figure 1: Microstructural aspects of copper slag from Paranapanema

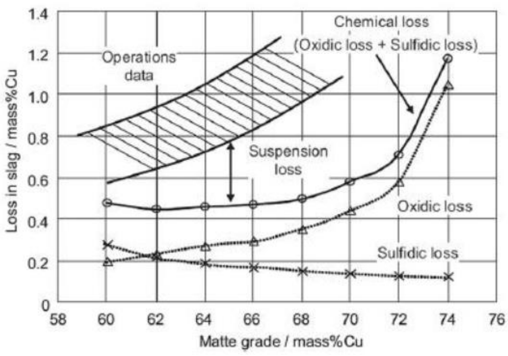
	
SEM image at 60X Content in the points: A 73 Cu 20 S 3Fe 0,6Si B 75 Cu 20 S 4Fe 0,6Si C 0,9 Cu 0,9 S 60Fe 22 Si	SEM image at 2000X Content in the points: A 67 Cu 21 S 10 Fe 0,3Si B 77 Cu 18 S 3 Fe 0,6Si C 1,2 Cu 0,8S 60Fe 21 Si D 1,4 Cu 1,1S 60Fe 22 Si

Source: The authors, 2023

Through the microstructure it was observed that there are tiny grains of sulfide distributed throughout the fayalite and magnetite/hematite matrix. Iron is in the form of silicate (fayalite) or in the form of oxide (maghemite). As suggested by this characterization report, it appears to be possible to release the sulfide and recover the copper by physical means using flotation. However, good release can only be achieved at a very fine size.

Based on figure 2, the loss of Cu occurs through oxides and sulphides. For this example, thermodynamically calculated data is presented in comparison with data from a foundry. According to this estimated reference, for a 62% matte grade, the proportion of sulphides and oxides would be 50%. And, according to a thermodynamic model, with an increase in the matt degree, the predominance of loss is by copper oxides [4].

Figure 2 – Loss of Cu in the slag as a function of the matte grade: data from one operation (foundry) and estimated from a thermodynamic model for oxides, sulphides or combination[4]

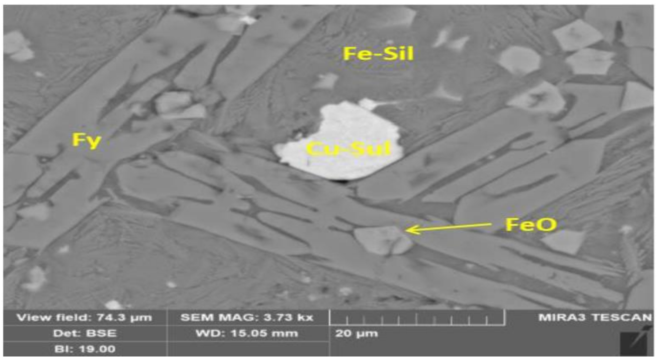


Source: Davenport, 2011

3.1.1 Flotation

The conventionally accepted route for processing copper sulfide minerals is flotation [4]. The fact is that under normal conditions the tests show that they are capable of releasing the sulfide and recovering the copper by physical means by flotation. As seen in the SEM images of Figure 3, the mesh of approximately 11 µm is the one for which 80% of the high copper content particles are released (P80 = 11 µm), that is, from this point of view, a very fine grinding fine is required for copper recovery.

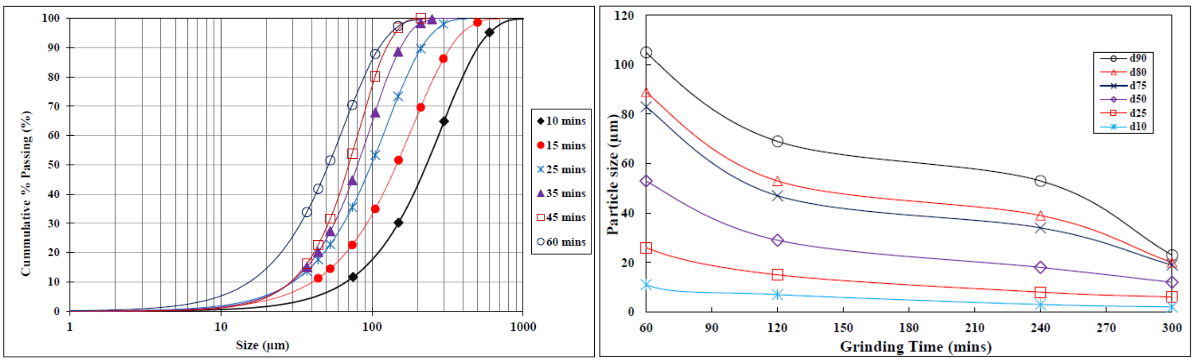
Figura 3: SEM image – copper sulfide particle with approximately 11 µm



Source: The authors, 2023

From the knowledge of the WI it is possible to define the energy consumption in the grinding of copper slag with a value of 28kWh/t. For comparative purposes, the value is much higher than that of copper ore, which presents WI values close to 14 kWh/t. Therefore, a high degree of comminution is mandatory to reach granulometry values close to the release of copper sulfides, as can be seen in figure 4.

Figure 4: Milling time X Sample granulometry



Source: The authors, 2023

It took 60 minutes to reach a P80 of 100 µm and approximately 300 minutes of milling to reach a P80 of 20 µm. After the flotation tests, it was possible to recover 94% of copper for a particle with a particle size of 11µm.

Therefore, the method becomes technically viable, but due to the high time and energy in the comminution being greater than twice the values to obtain the copper concentrate via ore, the flotation for copper recovery in the slag has not been proven to be financially viable obtained with the copper ore itself.

3.1.2 Leaching

One of the most used industrial routes to obtain copper from oxidized materials is leaching. In conventional processes, an acid solution (H_2SO_4) is used as a leaching agent in the legacy of copper from weathered ores [4].

In this process, in addition to involving the same communication steps as the flotation process, a large volume of reagents is consumed, such as sulfuric acid, water, electricity and, mainly, the high generation of hazardous waste that needs to be classified or sent to industrial landfills, this route becomes economically unfeasible due to the number of steps and high processing cost.

3.1.3 Pyrometallurgy

Other alternative for processing copper slag is through melting in processes with the addition of coke and fluxes. In addition to recovering metals such as copper, an alloy with a high iron content is also formed that can be used for other applications.

Tests were carried out in the furnace that uses a submerged lance originally developed for melting materials and recovering metals in different phases called TSL (Top Submerged Lance). After the addition of coke, limestone, compressed air, natural gas and electricity, a temperature of 1450ºC was reached for approximately 6 hours, however, there was no formation of pig iron in the reduction steps and good separation between metallized phase and slag of the molten material was not observed.The main reasons are associated with the technology of the kiln obtained for the transformation of fayalite from iron silicate, short residence time for reduction of fayalite, insufficient heat input, previous chemical reaction not achieved, non-separation of phases due to the turbulence caused by the kiln operation and during tipping.

Other tests were carried out using an electric arc furnace with a slag melting time of 24 hours. And after adding coke and fluxes and reaching a temperature of 1350ºC, he partial separation of copper in the form of Mate and recovery shown in table 3 was verified.

Table 3: Electric Furnaces tests

Tests	Slag Copper content		% Copper recovery
Amount (ton)	Input	Output	
15,210	0,72%	0,45%	37,50%
57,661	1,95%	0,50%	74,36%
35,366	2,43%	0,46%	81,07%

Source: The authors, 2023

3.2 Other segments for the application of copper slag

As the metals present in the slag are in very small amounts, their recovery may not be economical by many processes. Therefore, its use in the production of different value-added products such as paving, abrasive blasting, asphalt, cement, concrete, cutting tools, tiles, glass, has been studied and its applications are being carried out worldwide [6,7].

The test carried out for the application of copper slag in the manufacture of ceramics and porcelain tiles, replacing feldspar and clays, as can be seen in table 4:

Table 4: Zero formulation percentage ratio and quantity purchased for raw material used.

Component	Zero Formulation (%)			
	Zero (% mass)	A (% mass)	B (% mass)	C (%mass)
Slag	0	10	20	30
white clay	31	27,7	24,4	21,1
kaolinitic clay	18	16,1	14,2	12,3
Feldspar	45	40,2	35,4	30,6
Limestone	1	1	1	1
Quartz	5	5	5	5

Source: The authors, 2023

In the visual aspect, the samples presented a smooth and shiny surface with a intense red coloring. And In physical terms, the addition of copper slag to the porcelain tile avoided both porosity and water absorption, reaching a minimum value of 0.36%, meeting the requirements for technical porcelain tiles. The general level of water absorption also indicates that the elimination optimized the sintering process, helping to achieve of its final stage. Density was also lower, which may result in more levels that, considering industrial production, can significantly reduce such as carbon emissions from transporting products. In short, this material demonstrates its potential for use in porcelain tile matrices, as most of its relevant thermal events occur in a temperature range to the other constituents of the referred product.

The temperature of 1200 °C meets the requirement for the manufacture of ceramic bodies in terms of formed phases and as already mentioned above, physical indices. However, an environmental assessment of the porcelain tile produced will be required.

4. CONCLUSION

In this paper, the technical viability of the application of copper slag was discussed through studies and tests, the results presented compatible or superior characteristics for use as raw material in several other products. In addition to the cost being relatively cheaper compared to conventionally used materials.

The tests carried out with the greatest potential for future applications were the use of slag to recover copper in an electric furnace and the technical feasibility of using it in the production of porcelain tiles.

The use of copper slag in nobler products is essential to eliminate the generation of new landfills, reduce the exploitation of natural materials and reduce expenses in metallurgical processes with destination and storage.

With the application of copper slag in various segments, it is also possible to significantly reduce CO2 emissions in the construction sector, as well as other environmental impacts. Therefore, it is evident that the use of copper slag is of paramount importance in the current management of industrial waste.

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