Synthesis of Commercial Products from Copper Wire-Drawing Waste

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Copper powder and copper sulfate pentahydrate were obtained from copper wire-drawing scale. The hydrometallurgical recycling process proposed in this article yields a high-purity copper powder and analytical grade copper sulfate pentahydrate. In the first stage of this process, the copper is dissolved in sulfuric acid media via dismutation of the scale. In the second stage, copper sulfate pentahydrate is precipitated using ethanol. Effects such as pH, reaction times, stirring speed, initial copper concentration, and ethanol/solution volume ratio were studied during the precipitation from solution reaction. The proposed method is technically straightforward and provides efficient recovery of Cu from wire-drawing scale.

INTRODUCTION

The importance of the copper industry has been increasing since the early 20th century until today due to increased demand for electricity, which in turn involves the installation of large power generators, transmission lines, and power distribution.

Considerable interest in synthesizing copper powder has increased in recent years because of its high electrical conductivity, relatively higher melting point, low electrochemical migration behavior, and excellent weldability.

Accordingly, and because of the reduction in raw material, the industry's future lies in improving production and costs, which means process optimization. The rolling and drawing of copper wire generates a residue, scale, which contains a very large amount of Cu and which may be considered a by-product. It is currently necessary to find alternative ways to exploit such products.[1–7]

The aim of this article is to find an alternative process for producing ultrafine copper powder and copper sulfate pentahydrate from this mill scale.

The principal methods for producing copper powders are electrolytic deposition at high current densities and the atomization of molten metal, the latter being used more to produce copper-alloy powders. Copper powders are also formed by cementation or reduction precipitation from aqueous solutions, but such precipitates are of little commercial interest.[8]

Copper sulfate is a highly versatile chemical with an extensive range of uses in industry, being mainly employed in agriculture as a protective fungicide (Bordeaux mixture), as an algaecide, and as an herbicide. It is likewise used to correct copper deficiency in soils and in animals, etc.

It is also currently employed in many industrial processes. The metal industry uses large amounts of copper sulfate as an electrolyte in copper refining. The mining industry employs it as an activator in the concentration by flotation of lead, zinc, cobalt, and gold ores. The paint industry uses it in antifouling paints, and it plays a part in the coloring of glass.

EXPERIMENTAL PROCEDURES

Characterization of Wire-Drawing Scale

This study used wire-drawing scale from a Spanish copper plant. To determine the degree of homogeneity of the waste generated in the plant, several samples were taken on different days and subsequently characterized.

First, samples were placed in a stove at 50°C for 48 h to determine the moisture content and then in an oven at 300°C for 2 h to determine the lubricant content. After dissolution, the copper content of different samples was analyzed by titration using 0.02 M ethylenediaminetetraacetic acid (EDTA) and polyacrylonitriles (PAN) as an indicator. Impurities from the samples were determined by atomic

absorption spectroscopy (PerkinElmer AAnalyst 200, Table I).

The mineralogical composition was examined by x-ray diffraction (XRD) analysis (Phillips PW1430 system with CuKα radiation, Fig. 1). Particle size distribution was determined by screening, the results of which are given in Table II.

Leaching

The first stage comprises the acid leaching of the waste using sulfuric acid, followed by filtration. The dissolution of the wire-drawing scale (Cu_2O, CuO) with sulfuric acid is characterized by the natural dismutation of Cu_2O according to reaction (1).[9]

The chemical reaction between the wire-drawing scale and sulfuric acid is as follows:

$$Cu_2O + 2H^+ = Cu^{2+} + Cu + H_2O. \qquad (1)$$
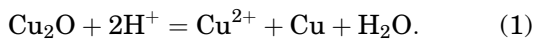
Table I. Chemical composition of wire-drawing waste

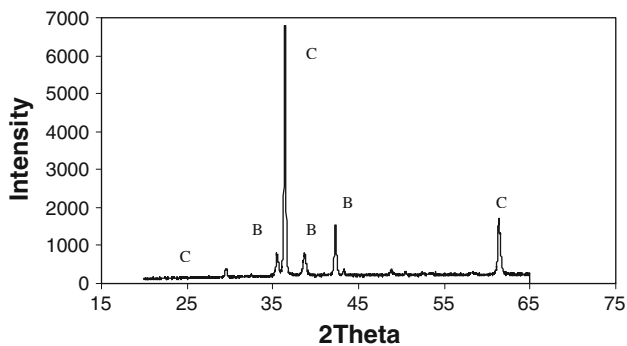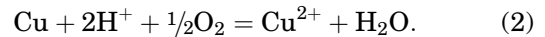|	A	B	C	D	E	F
% Moisture	6.67	9.68	6.75	6.34	6.54	6.23
% Lubricants	0.2	0.27	0.2	0.2	0.2	0.2
% Cu	90	89	90	89.5	89	89
% Fe	0.03	0.03	0.03	0.03	0.02	0.03

Fig. 1. XRD patterns of the scale F. C—Cu_2O; B—CuO.

The metallic copper thus formed was subsequently dissolved in the presence of air according to the reaction:

$$Cu + 2H^+ + 1/2O_2 = Cu^{2+} + H_2O. \qquad (2)$$

The small amount of CuO in the scale was dissolved according to the following reaction:

$$CuO + 2\,H^+ = Cu^{2+} + H_2O. \qquad (3)$$
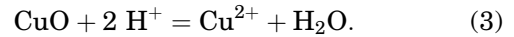
Experiments were carried out in a batch heater reactor vessel equipped with a mechanical stirrer. For each test, the reactor was charged with the sample and the H_2SO_4 (30% mass) leaching solution and the mixture was vigorously stirred at 500 rpm. Solution samples were withdrawn and filtered, determining the copper content in the resulting liquor via titration with 0.02 M EDTA.

Time (5–240 min) and temperature (20–100°C) were varied to study the effect of these parameters on copper leaching.

The aim of this study is the reuse of this scale at the lowest process cost. Therefore, in this first step, only the dismutation reaction of Cu_2O and the dissolution of CuO are performed.

Several tests were carried out using between 30 g and 150 g of scale, adding water and the amount of concentrated sulfuric acid needed for the dismutation reaction in each case. After 15 min of reaction, the solution was decanted in each assay and the copper concentration was determined to calculate the percentage of copper recovery.

The result of the dismutation reaction is a liquor rich in copper sulfate and copper powder. This copper is very reactive and tends to oxidize in air. Therefore, the solid residue that is generated in the reaction was washed several times with a 1% (mass) solution of benzoic acid and then rapidly filtered and introduced into an Erlenmeyer flask with an adapted plug to allow the introduction of nitrogen (inert atmosphere). This device was located inside a stove at 50°C to dry the sample.[10]

Table II. Scale particle size distribution

Fraction	A (%)	B (%)	C (%)	D (%)	E (%)	F (%)
>1 mm	0.08	0.09	0.15	0.16	0.29	1.21
1–0.5 mm	6.06	8.07	4.20	5.36	9.27	15
500–300 μm	25.81	27.63	19.49	27.96	29.11	26.1
300–150 μm	31.09	30.71	24.21	33.76	31.10	28.31
150–100 μm	12.79	12.46	13.77	13.83	11.44	11.01
100–75 μm	6.44	7.00	14.50	6.70	6.01	6.16
75–45 μm	12.15	8.96	16.02	8.54	8.09	5.96
<45 μm	5.57	5.07	7.67	3.69	4.70	4.9

The copper sulfate solution was subsequently used to produce copper sulfate pentahydrate.

Preparation of Copper Sulfate Pentahydrate

Aqueous precipitation is one of the most important unit operations in hydrometallurgical processes.

The optimal precipitation parameters were determined by evaluating the effects of different factors: time (5–25 min), stirring speed (100–500 rpm), solution pH (1.7–3.4), initial copper concentration (6.7–86.4 g/L Cu), and ethanol/solution volume ratio (0.5–2.5). For each experiment, 25 mL of copper sulfate solution were used to precipitate copper sulfate pentahydrate. At the end of each test, a solid/liquid separation was performed and the copper content remaining in the liquid was determined using 0.02 M EDTA. Finally, the percentage of precipitated copper was calculated.

Product Characterization

The characterization of the copper powder was performed using different techniques: chemical composition and morphology by scanning electron microscopy (SEM) and specific surface area determined by the Brunauer–Emmett–Teller (BET) method.

The copper sulfate pentahydrate obtained by crystallization in the second stage of the process underwent several tests: x-ray diffraction and thermal and chemical analysis; Cu was determined by titration with EDTA after dissolution; and impurities, by atomic absorption.

RESULTS AND DISCUSSION

Characterization of Scale

Table I shows the great similarity of the six tested samples. A high Cu content, of around 90%, is observed in addition to very slight contamination with iron, 0.03%.

The particle size of the scale ranged mainly between 500 μm and 45 μm (Table II).

Figure 1 shows the XRD patterns of the waste. Cu_2O was the main phase detected in the waste, the presence of a lesser proportion of CuO also being detected. Only the XRD patterns of sample F are included in this figure due to the homogeneity of the waste. Different size fractions showed no change in crystal structure.

Leaching

Effect of Time

Assays were performed only with scale F. Figure 2 presents the results of extraction at room temperature using, in some cases, the stoichiometric amount of acid needed to dissolve one gram of scale and, in others, a 100% excess of acid.
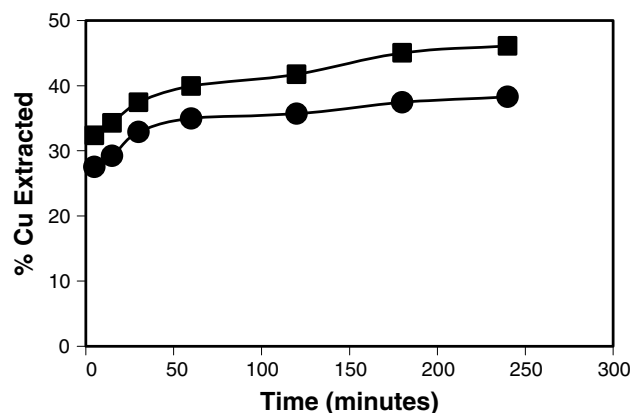
Fig. 2. Influence of reaction time on Cu extraction using different amounts of acid. ●—Stoichiometric; ■—100% Exc.
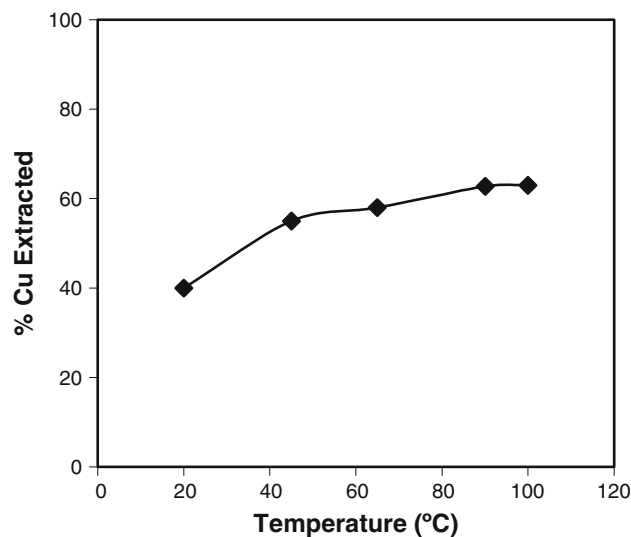
Fig. 3. Influence of temperature on Cu extraction.

The percentage of copper recovery using the stoichiometric amount of acid varies between 27.5% and 38.3%. Increasing the amount of acid used slightly improves the percentage of extraction. With an excess of 100% of acid, it can be observed that 32% of the copper dissolves after only 5 min of contact between the solid and the liquid. The subsequent leaching is much slower, however, obtaining only 46% dissolution after 4 h of reaction. This is because the dismutation reaction is very fast, while the dissolution of copper metal formed during the reaction requires a much longer time to enable the dissolution of atmospheric oxygen required for oxidation.[11]

Effect of Temperature

The effect of temperature was examined in the range of 20–100°C under the following conditions: 30% sulfuric acid concentration, 1 h of reaction,
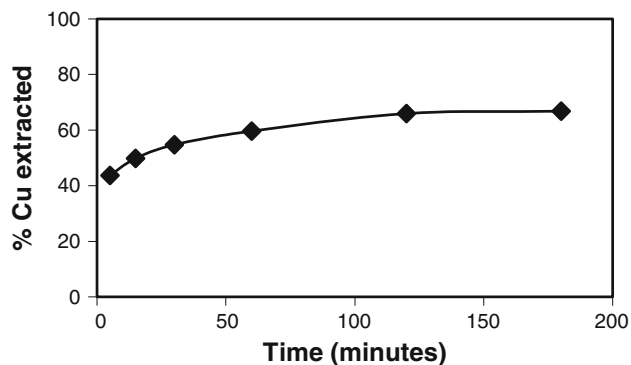
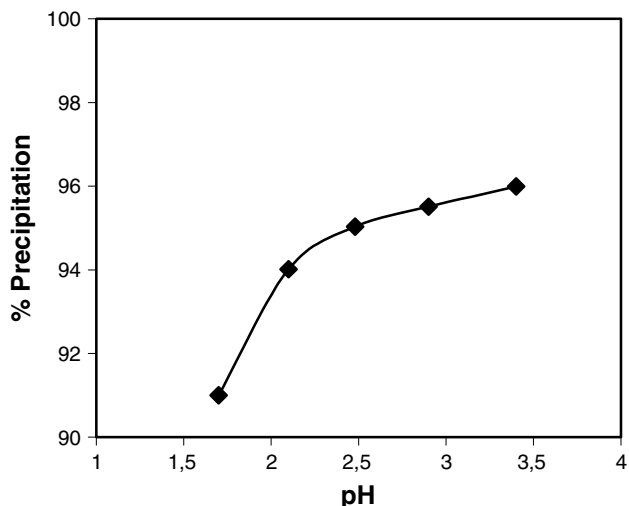Fig. 4. Influence of reaction time on Cu extraction at 45°C.

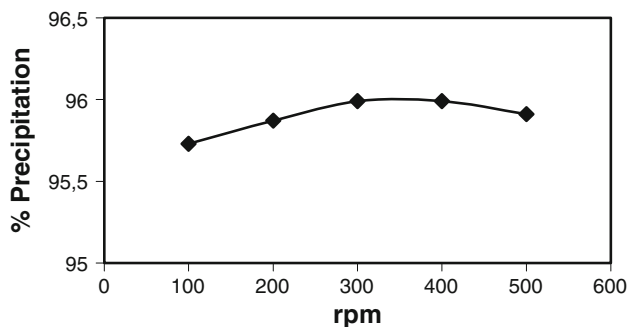Fig. 5. Influence of pH on copper sulfate pentahydrate precipitation.

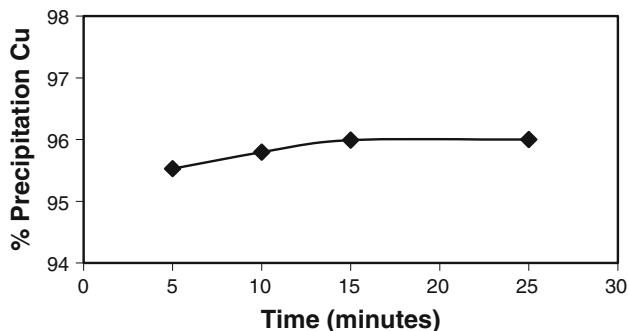Fig. 6. Influence of magnetic stirring rates on copper sulfate penta-hydrate precipitation.

Fig. 7. Influence of reaction time on copper sulfate pentahydrate precipitation.

500 rpm stirring speed, and a 100% excess of acid with respect to the soluble copper.

As shown in Fig. 3, copper recovery increased gradually with increasing temperature. Cu extraction after 1 h reached 39.94% and 63% for 20°C and 100°C, respectively.

As a value of extraction of around 50% is obtained at an intermediate temperature of 45°C, the effect of time at this temperature was also evaluated maintaining the parameters in the aforementioned tests constant: stirring speed of 500 rpm and a 100% excess of sulfuric acid (30%mass; Fig. 4). As shown in this figure, there is a significant increase in copper leaching when the test is performed at 45°C, the differences increasing with increasing reaction time.

It was decided not to prepare solutions of sulfuric acid previously but to use the latent heat of dilution to improve the dissolution of the copper.

Precipitation of Copper Sulfate Pentahydrate

Effect of pH Solution

The influence of pH on the precipitation of copper sulfate was tested to determine whether the amount of acid added in the leaching step could have a significant influence on copper sulfate precipitation. Overall, 30 g of scale were leached using the stoichiometric amount of sulfuric acid, while in other tests, an excess of acid was used. The pH of the resulting solutions varied between 1.7 and 3.4. The reaction conditions of copper sulfate precipitation were as follows: 26.7 g/L Cu, 300 rpm, 15 min of reaction, and (ethanol/sample volume) ratio = 1.

As shown in Fig. 5, increasing the amount of acid causes a slight decrease in copper sulfate recovery: 96% of the copper is recovered using the stoichiometric amount of acid, whereas copper recovery decreases to 91% when using an excess of acid. The concentration of free sulfate ions decreases when the amount of acid increases due to the formation of bisulfate ions.[12] Solutions with a lower pH contain HSO_4^-, which interferes in the formation of the $Cu-SO_4^-$ bond, thereby decreasing the efficiency of the precipitation.

Subsequent assays were performed with the stoichiometric amount of sulfuric acid (pH 3.4).

Effect of Magnetic Stirring Rates

Several magnetic stirring rates were employed ranging from 100 rpm to 500 rpm under the following operating conditions: 26.7 g/L Cu, 15 min of reaction, and (ethanol/sample volume) ratio = 1.
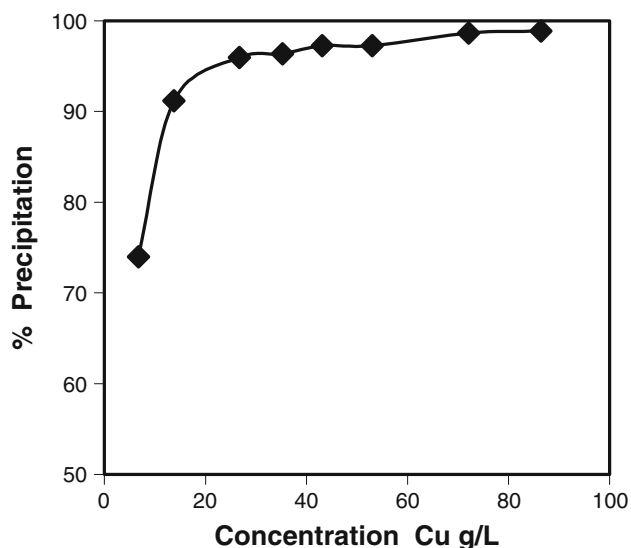
Fig. 8. Influence of copper concentration solution on copper sulfate pentahydrate precipitation.
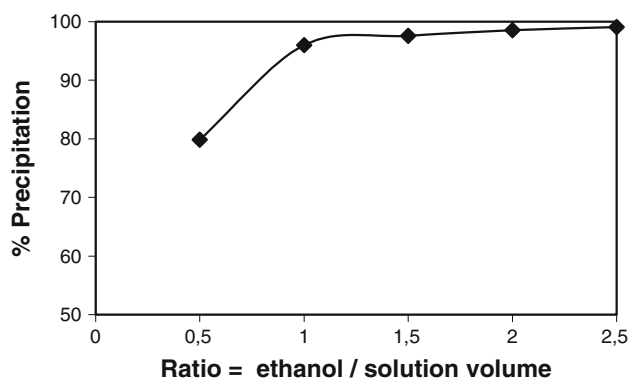

Fig. 9. Influence of ethanol/solution volume ratio on copper sulfate pentahydrate precipitation.

The effect of the magnetic stirring rate on copper sulfate precipitation efficiency is shown in Fig. 6. No obvious advantages were observed as the magnetic stirring rate increased from 100 rpm to 500 rpm, copper precipitation efficiency being greater than 95.7% in all cases. The maximum value was obtained at 300 rpm (96%). Subsequent tests were therefore performed at this stirring speed.

Effect of Time

Different tests were performed by varying the stirring time between 5 and 25 min under the following reaction conditions: 26.7 g/L Cu, (ethanol/sample volume) ratio = 1.

No significant variation was observed in the efficiency of the reaction, reaching 95.5% precipitation at 5 min and increasing to 96% after 15 min. Increased reaction time did not improve the efficiency of the precipitation (Fig. 7). For this reason, subsequent trials were carried out with 15 min of reaction.

Effect of Copper Concentration

Several copper sulfate solutions were performed by leaching different amounts of scale (30–150 g) with a stoichiometric amount of concentrated sulfuric acid and varying the amount of water added. These solutions were used to study the effect of the initial concentration on copper sulfate precipitation.

Initial solution concentrations varied between 6.7 g/L and 86.4 g/L Cu. In this case, the reaction conditions were as follows: 15 min of precipitation reaction, pH 3.4, and (ethanol/sample volume) ratio = 1.

According to the experimental results, precipitation increased with copper concentration (Fig. 8). In the test performed with a solution containing a low copper concentration (6.7 g/L Cu), only 74% Cu was recovered, while the assay carried with the higher concentration solution (86.4 g/L Cu) achieved an efficiency of 98.8% in the precipitation reaction.
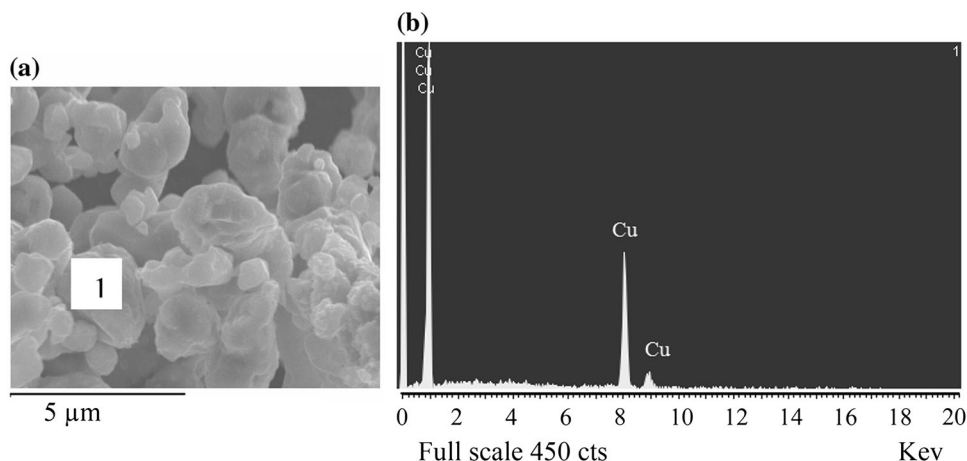

Fig. 10. (a) Scanning electron micrograph of Copper powder ×10,000. (b) EDS spectrum containing Cu 100%.

Effect of the Amount of Ethanol

Finally, several tests were performed with a solution of 26.6 g/L Cu to determine the influence of the amount of ethanol by varying the ethanol/solution volume ratio (0.5–2.5).

Figure 9 shows that copper sulfate precipitation reached 79% when using only a small amount of ethanol ($r = 0.5$) and that increasing the amount of ethanol led to improved results, obtaining 96% recovery with a ratio $r = 1$ and 99.1% with a ratio $r = 2.5$.

Ethanol behaves as a water-removing or dehydrating agent when added to sulphate solutions, reducing the solubility of copper sulfate.[13,14]

Product Quality

The two products obtained in this process, copper powder and copper sulfate pentahydrate, were characterized.

Characterization of Copper Powder

Figure 10 shows the SEM of the copper powder obtained in the dismutation.

This figure shows that the copper powder is made up of very small, more or less rounded particles with a chemical composition close to 100% Cu. The oxygen content (0.013%O) was analyzed by Oxygen and Nitrogen Analyzer ON-900. Note the great effectiveness of washing with benzoic acid and drying in

an inert atmosphere to prevent oxidation of the powder obtained by dismutation.

The specific surface area determined by the BET method was found to be 3400 cm^2/g.

Characterization of Copper Sulfate Pentahydrate

The copper sulfate pentahydrate was washed with fresh alcohol and subsequently dried under a vacuum at 45°C for 2 h. Figure 11 displays the XRD pattern of the final product, along with those corresponding to two commercial sulfates. The relative

Table III. Cell parameters of the final product, along with those corresponding to two commercial sulfates

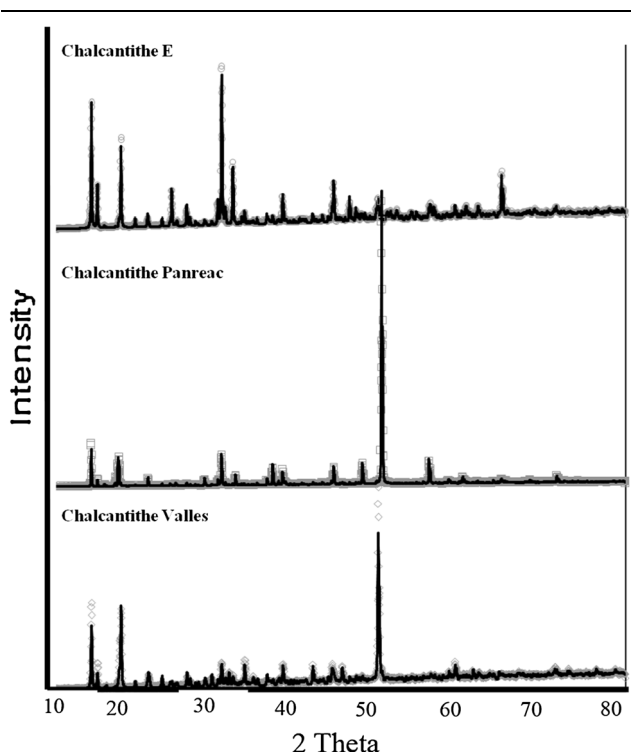| Simple	Crystal system	Cell parameters a, b, c α, β, γ	Volume [Å]³
Chalcanthite E	Triclinic	5.966 Å; 6.115 Å; 10720 Å 77.37°; 82.36°; 72.73°	363.5
Chalcanthite panreac	Triclinic	5.967 Å; 6.118 Å; 10.709 Å 77.50°; 82.46°; 72.66°	363.3
Chalcanthite valles	Triclinic	5.954 Å; 6.111 Å; 10.700 Å 77.45°; 82.48°; 72.70°	361.9

Fig. 11. XRD pattern of the final product, along with those corresponding to two commercial sulfates.
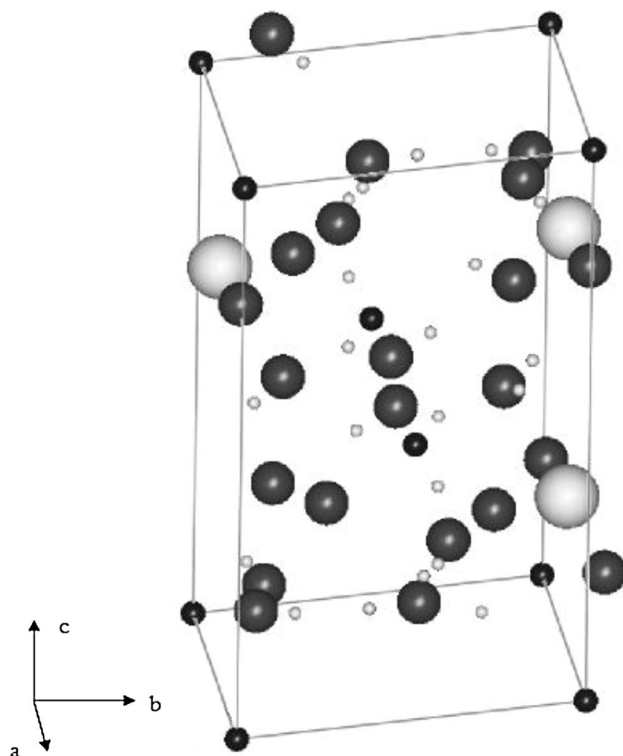

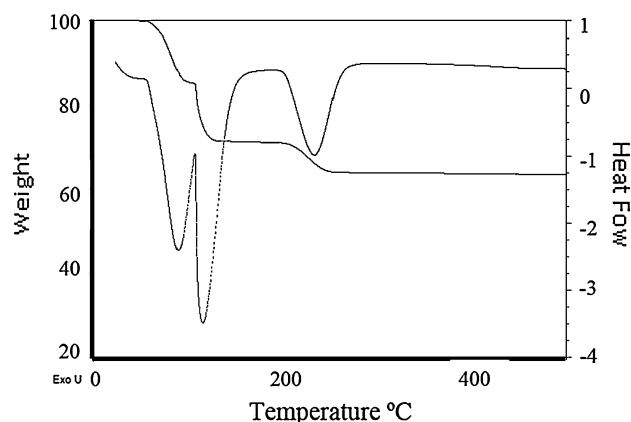Fig. 12. Crystal structure of obtained copper sulfate pentahydrate.

Fig. 13. TGA of the copper sulfate pentahydrate final product.

deflections of the x-ray diffraction diagram correspond to copper sulfate pentahydrate (Chalcanthite) in the triclinic system, as do the two commercial products. The cell parameters are shown in Table III, while Fig. 12 shows the crystal structure.

The thermal gravimetric analysis carried out showed that the product obtained is copper sulfate pentahydrate (Fig. 13). The decomposition spectrum clearly shows that the crystal starts to lose its water of coordination at around 86°C, according to reaction 4. It then loses another two molecules of water at close to 100°C (reaction 5), and completely dehydrates on heating it to ~232°C (reaction 6).

$$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O + 2H_2O, \quad (4)$$

$$CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot H_2O + 2H_2O, \quad (5)$$

$$CuSO_4 \cdot H_2O \rightarrow CuSO_4 + H_2O. \quad (6)$$

The EDTA titration resulted in a copper content of 25.46%. As expected, atomic absorption analysis showed that this is a very pure product, as the scale contains only a slight degree of iron contamination. Aktas[13] showed that the ethanol precipitation method is a selective precipitation of sulfates, leaving impurities in solution.

The copper sulfate thus obtained has a small particle size, of less than 0.5 mm, with more than 83% being less than 0.3 mm.

The copper sulfate pentahydrate obtained in this study was of analytical grade.

CONCLUSION

It is possible to treat scale to obtain different products with commercial grade characteristics: copper powder and copper sulfate pentahydrate. The copper sulfate thus obtained is of analytical grade.

The proposed method is straightforward. First, the scale is leached for 15 min with the stoichiometric amount of sulfuric acid and water to obtain copper powder and a concentrated solution of copper sulfate. After decanting the solution, the powder is washed with 1% benzoic acid solution and dried in an inert atmosphere. The copper powder thus obtained has a purity of 99.99%.

The second stage comprises the precipitation of copper as copper sulfate pentahydrate using ethanol. It has been shown that the reaction is very fast, with most of the copper present in the solution crystallizing after only 10 min or 15 min of stirring. Varying the stirring speed between 100 rpm and 500 rpm has virtually no effect on the reaction. It has also been shown that the factors that most influence the precipitation reaction are pH, initial copper concentration, and amount of ethanol.

With this method, greater than 96% of the copper in solution was recovered using concentrations higher than 26 g/L Cu with an ethanol/volume solution ratio = 1 and 3.4 pH.

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