ANODIC ELECTROLYTIC DISSOLUTION OF COPPER SULPHIDES PRECIPITATED FROM AMMONIACAL LEACHING MEDIA

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ABSTRACT

Anodic dissolution of synthetic chalcocite (previously obtained by copper precipitation with S and SO₂ in ammonia media) in two different electrolytic cells is described. One cell has a circular graphite anode placed horizontally, surrounded by a stainless steel cylinder as cathode, and the other has a rectangular basket-shaped graphite anode, with a rectangular stainless steel cathode placed in front of it.

The electrolysis was performed at 0.2 A and 50 °C, the electrolyte contained 20 to 40 g L⁻¹ of Cu and 100 to 160 g L⁻¹ of H₂SO₄, and the initial reactions took place at low potential (0.4-0.6 V) until the transformation of Cu₂S into CuS, detected by the considerable increase in cell potential. Anodic and cathodic efficiencies greater than 100% and 95%, respectively, were obtained. The high anodic efficiency is due to faradic and chemical dissolution too. It is also shown that the (CuS) produced as waste material can replace elemental sulphur as copper precipitating agent in ammoniacal media.

Keywords: Copper, anodic dissolution, copper sulphide, anodic graphite.

INTRODUCTION

Anodic dissolution.

Anodic dissolution of copper sulfides (such as copper concentrates or matte) is not a new idea. In 1882 Marchese¹ tried to apply this method to concentrates with low copper content, but problems with the cell's high tension, contamination of the solution with iron during electrolysis, and the bad quality of the cathodic deposit made him give up. New methods and techniques were developed in this field, such as the use of white metal anodes instead of concentrates, but the processes were not commercialized.

Habashi and Torres-Acuña⁶ used white metal anodes, mainly of Cu₂S, obtained by melting copper concentrates. They used sulfuric acid and cupric sulfate as electrolyte in the anodic dissolution and a copper sheet as cathode. At the end of the experiment, the composition of the solid residues was 80% elemental sulfur and 20% CuS, and the efficiency of the cathodic current was 98%. They proposed three stages for the anodic dissolution: first, conversion of Cu₂S to Cu_{1.98}S, followed by the formation of CuS, and finally dissolution as Cu²⁺ ions and formation of elemental sulfur (when working with low current density). The cathodic deposit obtained was comparable to that in conventional electrolytic refining.

Brennet et al.⁷ worked under galvanostatic and potentiostatic conditions using compressed Cu₂S powder as anode, and the anodic solution contained sulfuric acid. They found that current density increases rapidly at first, reaches a maximum, and then decreases, but never drops to zero. By X-ray diffraction they detected the existence of digenite (Cu_{1.8}S) during the early current density increase, then blue covellite (Cu_{1.1}S) appears when the current density decreases (depending on the anodic potential, because at high potential there is sufficient energy for nucleation of covellite -CuS), and finally dissolution as Cu²⁺ ions and elemental sulfur. The anodic potential also has an influence on the experiments because when it increases, the efficiency of the current decreases. Galvanostatic experiments were also made, with similar results in the anodic dissolution.

Anodic dissolution of Cu₂S was also studied by D.J. Mackinnon⁸ by the fluidized bed technique, which consists in allowing the electrolyte pulp and particles of Cu₂S to flow over an inert platinum anode, with the advantage that the anodic surface of this sulfide is larger per unit volume compared to conventional flat electrodes, because the sulfide is in powder form. When H₂SO₄ was used as electrolyte, 50% of the copper present in the sulfide was extracted, and later oxygen evolution was seen at the platinum anode.

Mackinnon found that the anodic dissolution using this technique took place in two stages: the first corresponds to the oxidation of Cu₂S to Cu_{1.1}S, and the second, which was detected due to the increase of the cell potential,

corresponds to the dissolution of Cu_{1.1}S as cupric ions and to the formation of elemental sulfur when H₂SO₄ - NaCl or H₂SO₄ - KBr was used as electrolyte.

Habashi and Torres-Acuña⁶, working with white metal anodes, confirmed the dissolution mechanism mentioned above by analyzing the residues obtained from different parts of the surface of the anode. It was also established that at low current density these residues contain more CuS than at high current density.

Mackinnon⁸, studying the intermediate products by X-ray diffraction and chemical analysis, showed that in the anodic dissolution of chalcocite (Cu₂S) under controlled current and potential conditions, and with a sulfuric acid electrolyte, the transformation is the following:

Later, the anodic potential increases noticeably, with oxygen evolution at the platinum anode, working galvanostatically, and the dissolved copper decreases and then remains constant. With the potential controlled sufficiently low as to avoid the release of oxygen, the current decreases substantially and the reaction becomes very slow, a result similar to that obtained by Habashi⁶ and Brennet⁷.

Peters⁹ confirmed the possibility of refining copper matte electrolytically from white metal if the latter is powdered, extracting 60% of the copper, and working with pure Cu₂S the extraction rises to 75% before anodic polarization occurs.

The anodic dissolution mechanism of Cu₂S is not as simple as shown by the authors mentioned above, because the reaction is more complex. Vitorge and Lamache¹⁰, who dissolved CuS₂ anodically, found Cu_{1.92}S, Cu_{1.77}S, Cu_{1.60}S and Cu_{1.31}S. Srinivasan et al.¹¹ showed that the electrochemical behavior and the products of the dissolution will depend not only on the conditions of the process, but also on the origin of the copper sulfide. However, it can be accepted that this takes place in two successive steps, with the tension in the cells increasing to 0.6 V in the first step and to 1.6 V in the second:

Guzmán et al.¹² proposed a method for obtaining electrolytic copper from copper concentrate through the following steps: sulfating roasting of copper concentrates at 700 °C; two leaching steps of the calcines at ambient temperature (in alkaline and acid media) with total recovery of copper in solution higher than 95%; precipitation of copper sulfide from the leaching solution with sulfur and sulfur dioxide; and finally, at the same time, anodic dissolution of the copper sulfide to obtain the copper at the cathode.

Hevia et al.^{13,14,15} have studied the precipitation of Cu with SO_2 and S in ammoniacal solutions at alkaline pH, achieving better than 90% Cu precipitation at ambient temperature. The overall reaction for precipitation in an ammoniacal environment is:

In the above equation it is possible to replace S by a copper sulfide material of the CuS type:

Methodology

The purpose of this work was to determine the behavior of the sulfide (Cu_2S), previously obtained by precipitation in an ammoniacal medium, in an anodic dissolution process, to obtain electrolytic copper at the cathode and a covellite-type residue at the anode. Electrolytes of similar composition and at the same temperature as those used in electrolytic cells for electrodeposition of copper in industry were used for the present work.

The anode material was graphite, whose good performance from the standpoint of corrosion has been shown because of the lack of Fe in the electrolytic system due to the low anodic potential of the process, which prevents the evolution of O_2 on the surface of the anode and the formation of S as an anodic residue. The anodic process continues until a covellitic residue (CuS) is formed, in order to prevent the increase of the anodic potential and the formation of S, since the latter is neither an electric conductor nor a semiconductor.

Obtaining Cu_2S

A sufficient quantity of S was added for a solution of 30 g L^{-1} Cu, 2 M total NH_3 , pH = 9.0, at ambient temperature, and excess SO_2 , until 80% of the copper precipitated. The precipitated sulfide containing 78.5% Cu, identified by X-ray diffraction, was mainly $\text{Cu}_{1.97}\text{S}$ (djurleite), and it was used in this study.

The different ways of obtaining Cu_2S are specified in a previous publication¹⁶.

Anodic dissolution.

Solutions containing 100 and 160 g L^{-1} of sulfuric acid, and 20 and 40 g L^{-1} of copper at a temperature of 50 °C were used as electrolytes. The anode was graphite and the cathode was a stainless steel sheet and an Ag/AgCl reference electrode. The copper sulfide in the precipitation (djurleite: 79.0% Cu) was introduced in the anode and the electrolysis was carried out under galvanostatic conditions, using a Hewlett Packard 6214-A power supply at a constant electric current intensity of 0.2 A. Two types of cells were used: A cell with a horizontal graphite anode in which the anodic compartment is cylindrical and it has a PVC structure covered with a filtering polyethylene sheet (diaphragm), and the cathode is a stainless steel cylinder whose mantle surrounds the anode compartment. The other cell has a vertical basket-shaped graphite anode and its cathode is a stainless steel sheet placed in front of the basket at a distance of approximately 5 mm.

Diagrams of these cells are shown in Figures 1 and 2:

Figure 1.- Cell with circular graphite anode.

Figure 2.- Cell with basket-shaped graphite anode.

RESULTS

Anodic solution with cylindrical graphite anode.

Three tests were carried out with this system under the conditions described in Table I. The results of the anodic electrodisolution are shown in Figure 3.

In the tests of this cell the aim has been to observe the phenomenon of anodic electrodisolution up to the stage of CuS formation and see the effect of the mass of precipitate on electrolysis time for different acid and copper concentrations in the electrolyte.

Table I - Cell with circular graphite anode.

Test		1	2	3
Initial Cu concentration	$\text{g} \cdot \text{L}^{-1}$	40	20	20
Initial acid concentration	$\text{g} \cdot \text{L}^{-1}$	160	100	100
Mass of chalcocite	g	2	5	14

Figure 3.- Experiments with circular graphite anode.

Anodic dissolution with basket-shaped graphite anodes.

The conditions of tests 4 and 5 are given in Table II; the difference between them is related to the way in which the basket was filled. In experiment 5 the chalcocite was compacted into the basket, while in experiment 4 it was not. Figure 4 illustrates these results.

In test 4 the basket was loaded by pouring the precipitate directly, and in the cell the electrolyte was poured slowly along the side of the basket. In test 5 the precipitate was poured directly into the basket, and the electrolyte was poured slowly over the precipitate in the basket, producing a compacting effect on the precipitate, whose height in the basket decreased 20%.

Table II.- Cell with basket-shaped graphite anode (compaction effect)

Test		4	5
Cell volume	mL	165	165
Initial copper concentration	g L ⁻¹	40	40
Initial acid concentration	g L ⁻¹	160	160
Initial mass of chalcocite	g	5	5

Figure 4.- Anodic electrodisolution experiments (compaction effect).

Table III gives the conditions of experiments 6 and 7, in addition to the previous experiment 5 (for comparison). These tests showed the effect of the quantity of chalcocite in the anode. Figure 5 illustrates these results.

Tests 6 and 7 were made in the same way as test 5, disregarding the effect of compaction and showing the effect of mass, which gives rise to self-compression.

Table III.- Cell with basket-shaped graphite anode (effect of amount)

Test		5	6	7
Cell volume	mL	165	165	130
Initial copper concentration	g L ⁻¹	40	40	40
Initial acid concentration	g L ⁻¹	160	160	160
Initial mass of chalcocite	G	5	9	10

Figure 5.- Experiments with basket-shaped graphite anode (effect of mass).

Each anodic dissolution experiment was carried out until the cell potential increase due to the formation of CuS was detected; copper extraction varied between 48% and 50% and copper residues of 64% were obtained. Identification by X-ray diffraction indicated covellite (CuS) as the main species, and no

elemental S was detected. The efficiencies of the anodic and cathodic currents were approximately 112% and 98%, respectively. The high anodic efficiency is due to faradic and chemical dissolution, both effects occur in parallel.

The performance of graphite as anodic material was as expected, and no corrosion or contamination of the cathodic Cu with C was detected. There was no evolution of oxygen at the anode, and neither was elemental sulfur formed, due to the control of electrolysis during the test.

The residue (of the CuS type) obtained from the anodic electrodisolution was reused to precipitate chalcocite (Cu₂S) in place of sulfur, a precipitation that is in agreement with Equation (5). Copper precipitation under these conditions is practically quantitative, and the final product corresponds to djurite (identified by X-ray diffraction).

For example, the 59.1% Cu residue, which was a polycrystalline solid –in which basically the covellite phase (CuS) was identified by X-ray diffraction– generated in the precipitation of copper in an ammoniacal environment, gave rise to a polycrystalline solid with 75.2% Cu in which the djurite (Cu_{1.98}S) and chalcocite (CuS) phases were identified by X-ray diffraction.

DISCUSSION

Figure 3, which corresponds to the experiments made with a circular graphite anode, shows a behavior of copper sulfide, obtained by the method of precipitation, similar to that described in the literature^{2,3,4,5} for the anodic electrodisolution of chalcocite, i.e., in the first stage the process is carried out at low cell potential (0.4 – 0.6 V) to obtain the CuS (Equation 2), and then that potential is increased considerably (up to 1.6 V) to extract a larger amount of copper and get sulfur as final product, in agreement with Equation (3).

The rectangular cell, similar to the industrial design for the electrorefining of copper process, and the basket-shaped anode showed a behavior of the anodic dissolution similar to that of the cell with a circular anode. The only significant difference is that for the small amounts of chalcocite used a prior compression was required to obtain the extraction yields close to 50% before the increase of the cell's potential, as shown in Figure 4. However, when using larger amounts of chalcocite this procedure was not necessary due to the natural compression caused by the weight of the particles, which allows good contact between them. The anodic dissolution achieved extractions close to 50% at cell potentials lower than 0.6 V, as shown in Figure 5.

The anodic current efficiency achieved before the cell potential increase, higher than 100%, shows that together with anodic dissolution there is chemical dissolution.

The process of precipitation of chalcocitic sulfide prevents the presence of an aggressive contaminant in the electrolysis, like the Fe and Cl present in the leaching solutions, in that way guaranteeing the life of the graphite anode in these electrodisolutions.

Controlling the process by means of the cell potential prevents the formation of S, so that the graphite does not become contaminated with that element.

In view of the characteristics of the process (which operates at low cell potential in order to reach the stage of formation of the covellite residues), the working potential is about 0.6 V, which prevents the evolution of O₂ on the graphite surface and its corrosion.

In all the experiments a cathodic deposit was obtained on the steel sheet, well adhered and without nodules.

There were no positive results either when using basket-shaped anodes or materials such as lead, iron, and stainless steel for that same anode support function.

CONCLUSIONS

It has been shown that anodic electrodisolution of copper sulfide is possible by the proposed precipitation method and that its performance is similar to that of the anodic electrodisolution of other copper sulfides described in the literature.

The results obtained with the cell with a basket-shaped graphite anode were very encouraging as to consider its implementation at the level of an

industrial process.

As expected, the residues (CuS type) of anodic electrodisolution can be used as agents for the precipitation of copper in an ammoniacal medium by replacing the sulfur.

This allows a proposal of a process for obtaining electrolytic copper from ammoniacal leaching solutions as shown in the following diagram:

Figure 6.- Summary flow diagram.

The innovative characteristics of the stages of this process (anodic precipitation and dissolution) make this proposal a clean technology for copper production.

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