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**CATALYTIC EFFECT OF ACTIVATED CARBON ON CHALCOPYRITE AND
ENARGITE LEACHING IN CHLORIDE MEDIA**

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ABSTRACT

Copper sulfides leaching have proven to be slow at atmospheric pressure therefore it is crucial to improve its kinetics for the purpose of becoming in a competitive alternative to the pyrometallurgical route. In order to enhance the leaching process, catalysts have been used such as activated carbon which has shown to have significant effect in sulfate media; nonetheless the catalytic mechanism of activated carbon in leaching processes of sulfide minerals is not well-understood yet.

The aim of this research was to evaluate the leaching of chalcopyrite and enargite in chloride media at 90°C under atmospheric pressure using activated carbon as catalyst considering speciation of copper, iron and arsenic in order to shed light on the mechanism of the activated carbon assisted leaching of sulfide minerals. On the other hand, four set of contact tests between synthetic PLS and activated carbon were performed with the purpose of proving the reduction and oxidation behavior of ions in the solution and the absorption of these in activated carbon and consequently have a more detailed insight on the catalytic mechanism.

The results presented in this study indicate that in the presence of activated carbon, copper recovery from the chalcopyrite concentrate and the enargite concentrate was 97% and 92% respectively after 96 h of leaching time. Based on the speciation results of leaching tests in the presence of the catalyst, first activated carbon reduced ferric and cupric ions and then activated carbon apparently helped to generate optimal condition that oxidize ferrous, cuprous and arsenite ions suggesting that catalyst behavior improved the leaching results

According to the contact tests between PLS and activated carbon, it was verified that the behavior of ions in the leaching tests was influenced by the presence of the activated carbon in the solution. Activated carbon was strongly affected by the presence of oxygen, temperature and pretreatment of the catalyst. Finally the absorption properties showed to be similar for copper, iron and arsenic at 80°C at different condition showing an adsorption of ions between 10% to 20 % although the absorption effect was apparently irrelevant in both enargite and chalcopyrite concentrate leaching tests due to its high copper recoveries which are not in accordance with the result of the contact test between PLS and AC.

RESUMEN

La lixiviación de sulfuros de cobre ha mostrado ser lenta en condiciones atmosférica, por lo que es crucial mejorar su cinética con el fin de convertirla en una alternativa competitiva a la vía pirometalúrgica. Con el fin de mejorar el proceso de lixiviación, se han propuesto el uso de catalizadores tales como carbón activado, el que ha demostrado tener un efecto significativo en los medios de sulfato, sin embargo aún no se conoce bien su mecanismo catalizador y como este funciona en un sistema de lixiviación de minerales sulfurados.

El objetivo de esta investigación fue evaluar la lixiviación de un concentrado de calcopirita y concentrado enargita en medio de cloruro a 90°C bajo condiciones atmosférica usando carbón activado como catalizador considerando la especiación de cobre, hierro y arsénico con el propósito de ahondar en el mecanismo del carbón activado en la lixiviación de sulfuros. Por otro lado, se realizaron cuatro pruebas de contacto entre PLS sintético y carbón activado con el propósito de probar el comportamiento de los iones en la solución y la absorción de estos en el carbón activado y en consecuencia tener una visión más detallada del mecanismo catalizador.

Los resultados indican que en presencia de carbón activado, la recuperación de cobre desde el concentrado de calcopirita fue de un 97% mientras que desde el concentrado de enargita fue de 92% después de 96 h. En base a los resultados de especiación de las pruebas de lixiviación en presencia del catalizador, primero el carbono activado reduce los iones férricos y cúpricos y luego aparentemente ayuda a generar condiciones óptimas que oxidan parcialmente iones en solución, sugiriendo que el comportamiento del catalizador mejoró los resultados de lixiviación.

De acuerdo con las pruebas de contacto entre PLS y carbón activado, se verificó que el comportamiento de los iones en las pruebas de lixiviación se vio influenciado por la presencia de carbón activado en la solución. El carbón activado se vio fuertemente afectada por la presencia de oxígeno, temperatura y pretratamiento del catalizador. Finalmente las propiedades de absorción mostraron ser similares para cobre, hierro y arsénico a 80 ° C a diferentes condiciones mostrando una adsorción de iones entre 10% a 20% aunque el efecto de absorción fue aparentemente irrelevante en las pruebas de lixiviación de enargita y calcopirita debido a sus altas recuperaciones de cobre, no estando en concordancia ambos resultados.

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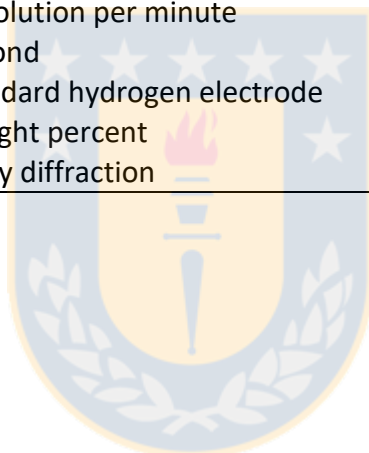
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SYMBOLS AND ABBREVIATIONS

AC	Activated carbon	
°C	Celcius degree	
DI water	Deionized water	
Eq.	Equation	
E	Equilibrium potential	mV
H	Hour	
L	Liter	
M	molar concentration	mol/L
m ²	Superficial area	
Min	Minutes	
N	Moles	mol
pH	Negative log of the hydronium ion molarity	
Ppm	parts per million	mg/L
RPM	Revolution per minute	
S	Second	
SHE	standard hydrogen electrode	mV
wt. %	Weight percent	%
XRD	X-ray diffraction	



1. INTRODUCTION

1.1 Background

Chalcopyrite (CuFeS_2) currently represents approximately 70% of the world's known reserves of copper and also is the principal source used for the production of metallic copper (Wang, 2005). The enargite (Cu_3AsS_4) which is a major carrier of arsenic is frequently associated with chalcopyrite (Padilla et al. 2005) being at times one of the main toxic impurities that can be present in a copper sulfide concentrate.

Pyrometallurgy has been the conventional process to treat copper concentrates because of its simplicity and economy. However the presence of important levels of toxic impurities and the current environmental regulations that restrict the emission of toxic gases into the atmosphere makes their treatment in smelters difficult and costly because it requires additional steps for the removal and safe disposal of pyrometallurgical residues.

Hydrometallurgical processes potentially offer considerable advantages over traditional pyrometallurgical processes because the impurities remain in the aqueous solutions being able to precipitate them into the form of an innocuous species and it can prevent the SO_2 production or/and emission becoming an eco-friendly alternative and finally for being an alternative at lower capital and operational cost. However lower recoveries in hydrometallurgical processes make most of these processes impractical thus it is important to enhance these rate of these processes in order to make them a competitive alternative.

One of the classifications of leaching processes can be grouped into: pressure leaching and atmospheric leaching processes. Pressure leaching are fast and efficient processes nonetheless they have a higher cost associated mainly with the use of autoclaves which is the main disadvantage. On the other hand, processes at atmospheric pressure can be carried out at lower capital and operational cost but usually have lower recoveries of copper (Padilla et al. 2008). It has been proposed the use of different oxidants, lixivants and catalysts for copper sulfide leaching with the purpose of improving dissolution rate at atmospheric conditions.

Researchers have studied the chalcopyrite and enargite leaching in sulfate media at atmospheric condition as a function of different variables where these minerals have proven to be refractory under atmospheric conditions. Chalcopyrite and enargite exhibit extremely slow kinetics product of their refractory behavior (Dutrizac1992). This drawback has been attributed to the formation of a passivating layer whose mechanism of formation and nature are still under discussion. To date, the literature is relatively limited with respect to enargite leaching and the majority of the studies have been focused on chalcopyrite leaching for both sulfate and chloride media.

The chloride media offers significant advantages over sulfate media promoting high metal solubility, enhanced redox behavior due to cupric and cuprous stability through complexation, lower sulfate formation and lower pyrite reactivity causing together higher dissolution rate of metals. Despite the advantages of chloride leaching, there has been a scarce progression toward commercial activity in the metallurgy industry due to problems with final product in terms of purity and morphology and for the necessary use of more expensive materials in reactors due to corrosive action of chloride ions (Watling, 2014).

An alternative to enhance the leaching rate of copper sulfides is the use of catalysts such as silver, pyrite and activated carbon. The literature about the use of activated carbon as a catalysis in hydrometallurgy is relatively scarce and most of these investigations are focused on the bioleaching of chalcopyrite. The few available studies have revealed that activated carbon considerably enhances the leaching rate of chalcopyrite and enargite in sulfate media. The mechanism of the catalyst effect of activated carbon is not completely known yet.

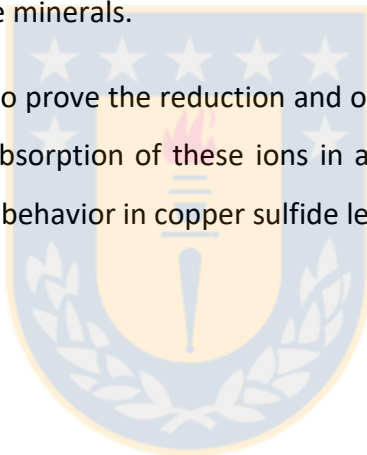
Several researchers have attributed this improvement to a possible galvanic interaction between chalcopyrite and enargite with activated carbon (Nakazawa et al., 1998; Zhang &Gu, 2007; Liang et al., 2010; Ghanad, 2011). On the other hand, some types of carbon are able to generate hydrogen peroxide (H_2O_2) in the presence of oxygen. The hydrogen peroxide can cause oxidation in the aqueous media which could help the leaching process. This phenomena is explained by the reaction of oxygen in the activated carbon surface (Ahumada et al. 2002). More recently this hypothesis has been corroborated by Choi et al., 2014; Radzinski & Ghahremaninezhad, 2015; Radzinski, 2017, who worked on the catalytic mechanism of activated

carbon during the oxidation process of As (III) to As (V). This latter hypothesis will be considered in this work to explain the results obtained in the activated carbon assisted copper sulfide leaching, nonetheless the connection of the surface chemistry in the catalyst and the leaching process of sulfide minerals is not well-understood yet.

1.2 Objective

The aim of this research was to evaluate the leaching of chalcopyrite and enargite in chloride media at 90°C under atmospheric pressure using activated carbon as catalyst considering the speciation of copper, iron and arsenic in order to shed light on the mechanism of the activated carbon assisted leaching of sulfide minerals.

A secondary objective was to prove the reduction and oxidation behavior of copper, iron and arsenic in the solution and the absorption of these ions in activated carbon with the purpose of increasing insight on the catalytic behavior in copper sulfide leaching.



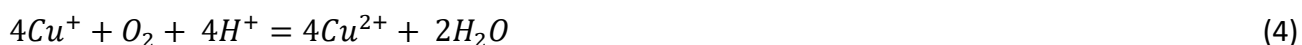
2. LITERATURE REVIEW

2.1 Acid Leaching

For several decades the leaching of chalcopyrite and enargite has been studied in acid solutions where usually the preferred lixiviant was sulfuric acid using ferric ions as an oxidizing agent to release copper into the solution. In some cases the addition of chloride ions in solution has been investigated in sulfate leaching or chloride media has been used itself which have shown to be more effective than sulfate media increasing the dissolution rate.

2.2 Chalcopyrite leaching in chloride media at atmospheric conditions

The chloride-based leaching of chalcopyrite has been studied extensively during the last 40 years. In all cases, a strong acidic oxidizing solution was required to release copper in the solution due to its refractory behavior (Dutrizac, 1992). Ferric chloride and/or cupric chloride have been commonly used and both have proven to be effective during the leaching at atmospheric pressure near the boiling point. The following reaction are generally accepted to describe the chalcopyrite leaching with ferric chloride and/or cupric chloride where for simplicity copper and iron species are written as simple cation in place of chloro-complex ions.



When ferric chloride is used as oxidant, chalcopyrite is reported to dissolve according to Eq. 1 and after a while it could take place Eq. 2 when the concentration of ferric ions and potential ions decrease (O'Malley and Liddell, 1987; Wang, 2005). On the other hand, when cupric chloride is utilized as oxidant, Eq. 2 is informed as the main reaction (Bonan et al. 1981; Lundström et al. 2005). When the leaching is carried out in the presence of oxygen or air, the produced cuprous and ferrous ions can partially be re-oxidized to cupric and ferric ions by oxygen respectively in accordance to Eq.3 and Eq. 4. The oxidation of cuprous to cupric ions is a fast reaction and the oxidation of ferrous ions is slow at ambient pressure, thus the regeneration of cupric ions can be

accomplished more efficiently than ferric ion regeneration at atmospheric pressure. Additionally other usual reaction in this system is when ferric ions also oxidize cuprous ions to obtain ferrous and cupric ions as shown in Eq. 5.

Elemental sulfur is the major sulfur product when chalcopyrite is oxidized with ferric chloride and/or cupric chloride as shown in Eq. 1 and Eq. 2. In this sense, Dutrizac (1990), and others studies have reported that the major sulfur product when chalcopyrite is oxidized in ferric chloride media is elemental sulfur reporting more than 95% of the sulfur product. Hirato et al. (1987) informed that the leaching with cupric chloride also produced a layer on chalcopyrite surface with a similar morphology to the layer produced during ferric chloride leaching.

Dutrizac (1981) and Majima (1985) determined that the leaching rate of the chalcopyrite in ferric chloride media is faster than in the ferric sulfate media. Dutrizac (1981) also found that the dissolution rate of the chalcopyrite increased with an increase in the concentration of ferric ions at all evaluated temperatures (65-95°C). O'Malley & Liddell (1987) pointed out that the oxidation of chalcopyrite by cupric ions has also been observed to take place in the last stage of ferric chloride leaching when the Fe(III)/Fe(II) ratio in the solution is less than 0.2 promoting an acceleration in the leaching rate.

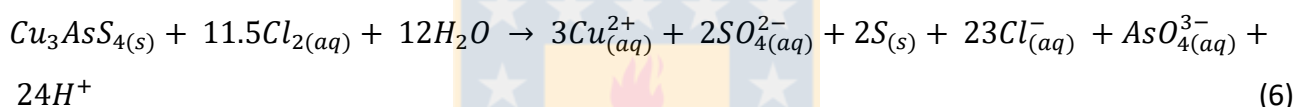
Chalcopyrite has been successfully leached in the presence of cupric ions as reported by Bonan et al. (1981), Wilson & Fisher (1981) and Lundström et al (2005), the leaching rate is strongly dependent on Cu(II)/Cu(I) ratio and chloride concentration in the solution. According to Bonan et al. (1981) the leaching rates showed to be high above 85°C when Cu(II)/Cu(I) ratios was maintained high. In accordance to Muir (2002), the dissolution of chalcopyrite is more advantageous with cupric chloride solutions compared to ferric chloride solutions due to higher rates of electrons transference, this is attributed to a greater speed and reversibility of Cu(II)/Cu(I) in relation to Fe(III)/Fe(II) on the surface of chalcopyrite.

To summarize, there are a number of factors that contribute to obtain an efficient and effective dissolution of chalcopyrite at atmospheric pressure such as concentration of oxidant and chloride ions, temperature, low pH and relatively fine particles size.

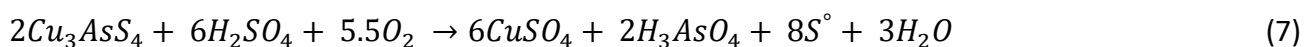
2.3 Enargite leaching in chloride media at atmospheric conditions

Chalcopyrite leaching serve as a reference to study the enargite leaching in the chloride media because to date literature about enargite is relatively scarce and the majority of the researches have been focused on chalcopyrite.

One of the first studies on enargite leaching using chlorine at atmospheric condition was carried out by Herreros et al. (2002). The study concluded that the kinetic of enargite leaching is characterized by two distinct reaction stages where the first stage is extremely fast controlled by diffusion through the liquid film, while the second stage is very slow controlled by diffusion through a solid product layer on the enargite surface which was believed to be composed of 50% elemental sulfur and 50% of sulfate. The reaction informed by these authors in the presence of Cl_2/Cl^- is presented in Eq. 6.



Padilla et al. (2005) have also studied the enargite leaching in 0.25 M H_2SO_4 - 1.5 M NaCl solutions using oxygen as oxidant under atmospheric conditions. The authors claimed that the dissolution proceeds according to Eq. 7 where more than 95 % of the sulfide was oxidized to element sulfur.



The most important parameter in this study was the sodium chloride addition which improved the dissolution rate of enargite with addition up to 2M as can be seen in Figure 1. Results indicate that dissolution rate of enargite in this media was very slow reaching only 6 % of arsenic extraction after 7 hours at 100°C.

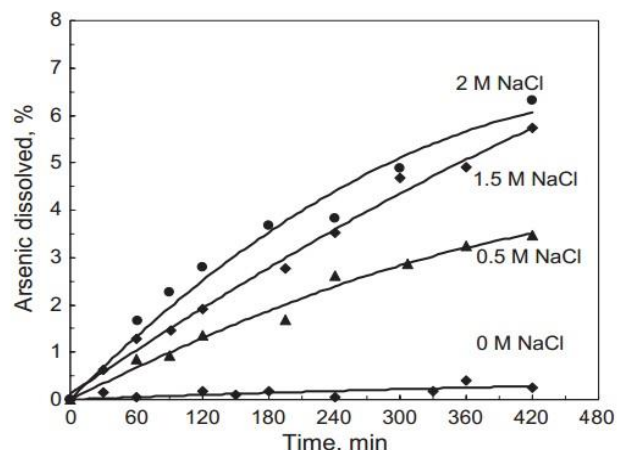


Figure 1. Effect of chloride concentration on arsenic dissolution from enargite in 0.25 M H_2SO_4 , 1.5 M NaCl, and 0.3 L/min of oxygen. (Padilla et al., 2005)

Using ferric chloride and hydrochloric acid media, Riveros and Dutrizac (2008) found that the enargite dissolution reaction is quite slow at temperatures below 100 °C. At 100 °C and after 16 hours, they obtained only 27% copper dissolution. The researchers observed that the copper dissolution rate was strongly temperature dependent and increased as temperature increased and was independent of the concentration of ferric chloride.

As already discussed above there are no doubts that the enargite dissolution rate is slow and strongly temperature dependant in chloride media under atmospheric conditions. The best results for enargite leaching were obtained at high temperatures and at high pressure or incorporating catalytic agents such as activated carbon using sulfate-based media (Padilla et al. 2008, Ghanad, 2011), chloride-based leaching have not been reported yet under the above conditions.

2.4 Thermodynamic aspects

In order to be able to determine the appropriate aqueous conditions for the dissolution of chalcopyrite and enargite, it is necessary to study the Pourbaix diagram which indicates the predominant species in solution and the solid intermediates solids phases present in the equilibrium with respect to the hydrogen ion activity and reduction potential. Hence, these diagrams indicate what adjustments in potential and/or pH are required to liberate the metal ions contained in the minerals. It is noteworthy to mention that the Eh-pH diagrams represent only the thermodynamic equilibrium and do not indicate which leaching pathway will be the most suitable or the kinetics of the involved reactions. The kinetic information must come from experimentation and must also be considered in the process design.

The Pourbaix diagram for the Cu-Fe-S-H₂O and Cu-Fe-S-Cl-H₂O system are shown in Figure 2. It can be seen from Figures 2.a and 2.b that when chloride ions is added to the Cu-Fe-S-H₂O system, this shows an area of stability for CuCl. From Figure 2, it is not possible to predict the predominant formation of elemental sulfur instead of sulfate species in chloride media, as has been reported from experimentation (Dutrizac, 1990; Dutrizac, 1992) who found that more than 95% of the sulfide sulfur oxidizes to elemental sulfur which did not affect the leaching rate under atmospheric conditions at temperature below 100°C.

The chalcopyrite dissolution in acidic media takes place thorough phase solid transformation in different intermediate copper sulfides such as bornite (Cu₅FeS₄), calcosine (Cu₂S) and coveline (CuS). The ideal conditions required for copper dissolution from chalcopyrite are potential greater than + 0.4 mV and pH lower than 4. These conditions are achieved using oxidizing agents such as ferric, cupric or chloride ions (Havlík 2008)

Padilla et al. (2008) carried out a thermodynamic study on the Cu₃AsS₄ –H₂O system obtaining Eh-pH diagram for this system at 25°C as presented in Figure 3. The authors point out that at lower oxidation potential between 0.4-0.58 V, enargite can thermodynamically dissolve to produce Cu²⁺, H₃AsO₃ and HSO₄⁻ for pH<2, and Cu²⁺, H₃AsO₃ and SO₄²⁻ for pH>2.

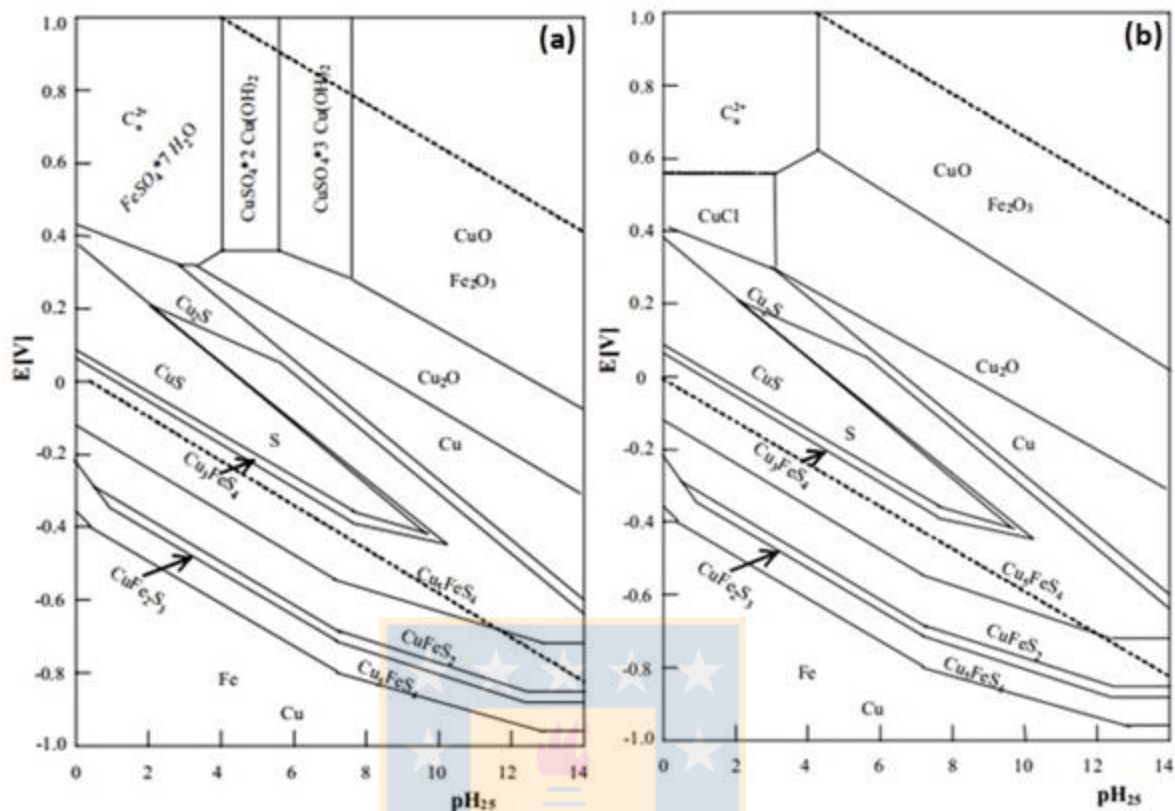


Figure 2. (a) Pourbaix diagram of Cu-Fe-S-H₂O system. (b) Pourbaix diagram of Cu-Fe-S-Cl-H₂O system. Both at 25°C, 1 atm and [Cu] = [Fe] = 10⁻³ M and [S] = 10⁻¹ M (Havlík, 2008)

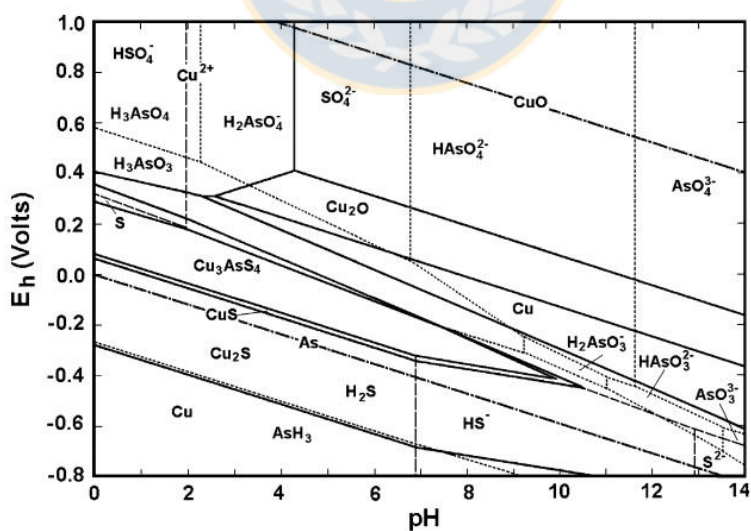
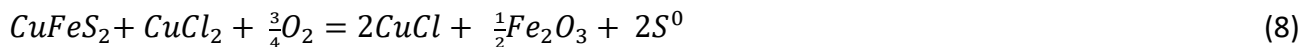


Figure 3. Pourbaix diagram of the Cu₃AsS₄-H₂O at 25°C for [Cu] = [As] = [S] = 0.1 M. S-H₂O equilibria are shown as dashed lines and As-H₂O equilibria as short dashed lines. (Padilla et al. 2008)

2.5 Chloride-based leaching processes at atmospheric pressure.

HydroCopper™ process

The HydroCopper™ process (Hyvärinen & Hämäläinen, 2005) was developed by Outokumpu. The process leaches chalcopyrite concentrates using cupric chloride and oxygen as oxidant and high concentration of sodium chloride according to the main reaction 8. The obtained solution then goes to the purification step where is treated with sodium hydroxide to precipitate cuprous oxide. This solid is filtered and reduced by hydrogen gas to metallic copper powder, which is melted to produce the final product.



Intec process

The Intec process is used for the extraction of pure copper and precious metals from sulfide concentrates. This process considers four-stage leach with chloride and bromide solution at atmospheric pressure where heat is provided by the exothermic leach reactions. First gold and silver are recovered using carbon filter and cementation with mercury ions respectively on the other hand, impurities in the solution are precipitated with lime and recovered by filtration. Lastly the purified copper liquor is electrowon to produce pure copper metal. During the electrowinning, the halide solution is regenerated at the anode which shows powerful leaching characteristics when is re-used to treat the incoming concentrates. The extraction of copper is approximately 98.5% and is achieved in 12 to 14 hours (Wang, 2005).

CUPREX process

The CUPREX process leaches chalcopyrite concentrates with ferric chloride solution at atmospheric pressure in two stages, supplying oxygen to re-oxidize Fe(II) and/or Cu(I). Then this solution is purified in the solvent extraction stage where is contacted with an organic solution and finally the concentrated aqueous solution of copper chloride is sent to electrowinning to produce granular copper. This process reports problems with the purity and morphology of the final product related with the chloride media (Wang, 2005).

CLEAR process

The CLEAR process treats copper concentrates in a two leaching stage. The first one used a leach solution composed by cupric chloride, ferric chloride, sodium chloride and potassium chloride at 107°C in order to produce a cuprous ion solution. The second stage consists in a leaching to a low oxygen pressure at 140 ° C. Subsequently copper is obtained by electrowinning of cuprous ions. This process reports problems with the final product because it does not meet the LME specifications (Wang, 2005)

Cuprochlor

The Cuprochlor process was patented by Michilla mining-Chile, this process offers greater efficiency in the recovery of fine copper over traditional leaching processes in heaps treating secondary copper sulfides such as chalcocite, covellite and bornite. The process consists in modifying the agglomeration stage in the leaching process through the addition of calcium chloride, sea water and sulfuric acid. The added calcium chloride reacts with sulfuric acid to form gypsum and chloride ions. Gypsum acts as a binding agent for the ore particles enhancing the agglomerate properties. Besides the chloride ion formation stabilizes cuprous ions and improved the regeneration of ferric ions .The copper recovery is nearly 93% and is achieved from 100 to 110 days against the 1 year required by the bacterial leaching processes (Aroca et al. 2012)

3. ACTIVATED CARBON

3.1 Activated carbon definition

The activated carbon term is used to refer to a wide range of quasi-amorphous materials based on carbon which exhibit a high degree of porosity and a large surface area (800-2500 m²/g). Activated carbon is not uniquely characterized by a specific structural formula or by chemical analysis. As a raw material, any substance with high carbon content and a low amount of inorganic material can be used as an activated carbon precursor. The uses of wood, fruit shells, and walnut or coconut shells have been reported (Marsden & House, 2006). Activated carbon has been extensively researched and has been used in many industries due to its catalytic and absorption properties. One of the main industrial uses in metallurgy is related to the extraction of gold and silver from cyanide solutions (McDougall & Hancock, 1981).

3.2 Activated carbon properties

Activated carbon is a porous material which share common characteristics with graphite but differ in their structures. Figure 4 illustrate the ideal structure of graphite and the proposed structure for activated carbon, where in the case of graphite this shows to be a highly ordered structure which consists of sheets of hexagonal carbon that stay together due to Van der Waals forces that maintain the carbon layers at a distance of 0.335 nm (McDougall & Hancock, 1981). On the other hand, the structure of activated carbon shows to be disordered which is characterized for containing small regions of crystalline/graphite structures that exist randomly oriented within disordered regions of carbon. (Marsden & House, 2006)

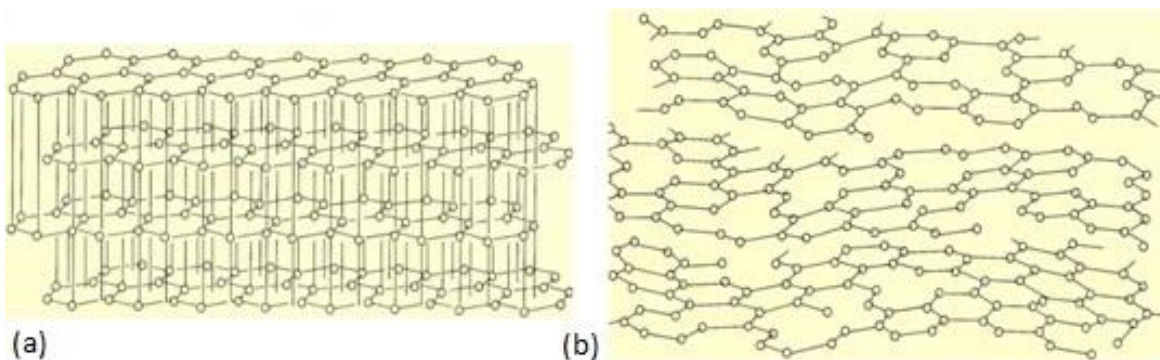


Figure 4. (a) Ideal crystalline structure of graphite. (b) Structure of activated carbon (McDougall & Hancock, 1981)

For the production of activated carbon, the raw material must be exposed to a carbonization process at high temperature (800°C-1000°C) in the presence of oxygen or air which reacts with carbon to release carbon monoxide and carbon dioxide leaving an extremely porous material with a large surface area. Although, carbonization produces a porous structure, it is sometimes considered rudimentary; thereby the physical activation is usually followed by a chemical activation treatment based on an oxidizing agent (Marsden & House, 2006).

Due to the high level of structural imperfection in activated carbon, during the activation process the edge carbon atoms react on the surface forming oxygen functional groups which are the most important in terms of influence on the surface properties of activated carbon. Oxygen is preferentially absorbed on the surface of the activated carbon compared to other elements, according to Marsden & House (2006) estimated that 90% of the oxygen present on the carbon surface exists as a variant of a functional group such as carboxyl, hydroxyl, carbonyl and ester groups. The structures of some oxygen-containing functional groups that exist on the carbon surface are presented in Figure 5.

The role of the chemical surface properties of the activated carbon has received considerable attention because it is a key factor to determine its behavior in different applications. Chemical Activation using different oxidizing agents has been reported in the literature such as nitric acid, hydrogen peroxide and ammonia persulfate by means of which the concentration or type of functional groups on the activated carbon surface can be changed affecting its behavior as absorbent or as catalyst.

The nitric acid treatment in aqueous media causes a slight acid nature and the formation of nitrogen containing functionalities. In addition to the formation of nitrogen functionalities groups, nitric acid treatment can increase oxygen functionalities concentration (Figueiredo et al 2006).

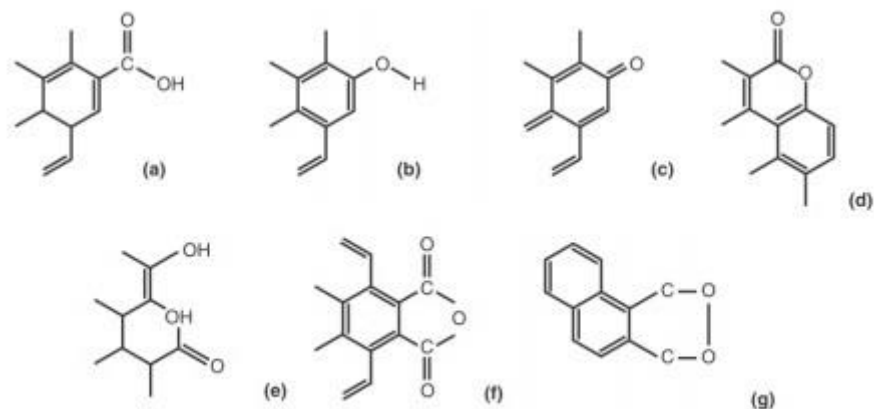


Figure 5. Surface oxide structures: (a) carboxylic acid, (b) phenolic hydroxyl, (c) quinone-type carbonyl groups, (d) normal lactones, (e) fluorescein-type lactones, (f) carboxylic acid anhydrides, and (g) cyclic peroxides (Marsden & House, 2006)

The pH of the solution where the activated carbon is suspended has a great influence on the surface charge of the activated carbon. In this sense, the electro-kinetic effect has a strong influence on the interaction between particles suspended in solution and the activated carbon. This effect can be quantified by measuring the zeta potential which represents the energy difference between the surface of a particle suspended in solution and the bulk of the liquid. The zeta potential will affect which functional groups exist on the carbon surface and which ions will preferably adsorb onto the carbon.

To summarize, the activated carbon can reduce some compound depending on the condition and availability of certain functional groups. The properties of activated carbon are dependent on the type functional groups, their concentration and distribution, oxygen availability, and pretreatment in activated carbon (Figueiredo et al. 2006).

Other important phenomenon to consider when using activated carbon is the absorption on its surface which mainly depends on the wide distribution the pore sizes in activated carbon. The absorption of metal ions on the activated carbon surface from aqueous solutions is also affected by the pH of the solution. As reported by Park et al. (2007) the copper ion adsorption increased as the solution pH increased from 1.5 to 6.

3.3 Activated carbon as catalyst

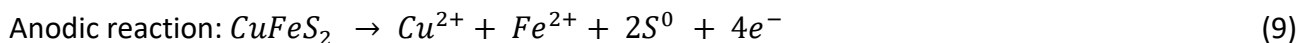
The literature about the assistance of activated carbon as a catalysis in hydrometallurgy is relatively scarce and most of these investigations are focused on the bioleaching of chalcopyrite. The few available studies have revealed that activated carbon considerably enhances the leaching of chalcopyrite and enargite in sulfate media. The researchers have attributed this improvement to a possible galvanic interaction between chalcopyrite and enargite with activated carbon (Nakazawa et al., 1998; Zhang & Gu, 2007; Liang et al., 2010; Ghanad, 2011).

However the mechanism of the catalyst effect of activated carbon is not completely known yet. On the other hand, some types of carbon are able to generate hydrogen peroxide (H_2O_2) in the presence of oxygen. The hydrogen peroxide can cause oxidation in the aqueous media. This phenomena is explained by the reaction of oxygen in the activated carbon surface (Ahumada et al. 2002). More recently, this hypothesis has been ratified by Choi et al., 2014; Radzinski & Ghahremaninezhad, 2015; Radzinski, 2017, who worked on the catalytic mechanism of activated carbon during the oxidation process of As (III) to As (V). This latter hypothesis will be considered in this work to explain the results obtained in the activated carbon assisted copper sulfide leaching.

3.3.1 Possible galvanic interaction

Nakazawa et al. (1998), Zhang & Gu (2007) and Liang et al. (2010) investigated the effect of activated carbon on the bioleaching of the chalcopyrite concentrate using different types of bacteria. All authors reported an improvement in the dissolution rate of chalcopyrite using activated carbon. Nakazawa et al. suggested that the improvement can be attributed principally to a galvanic interaction between activated carbon and chalcopyrite, which means that chalcopyrite could have acted as anode and consequently dissolved while activated carbon could have acted as a cathode and therefore, Eq. 9 and Eq. 10 may have occurred in the process.

Zhang & Gu (2007) and Liang et al. (2010) also stated that the catalytic effect of activated carbon was due to a possible galvanic coupling with chalcopyrite.



Ghanad (2011) and Dixon & Rivera-Vásquez (2012) studied the activated carbon catalysis of enargite leaching in ferric sulfate media. It was demonstrated that the leaching was up to 6 times faster in the presence of the catalyst. The proposed hypothesis by Ghanad (2011) was similar to the mechanism used to explain the catalytic effect of activated carbon on bioleaching (Nakazawa et al. 1998).

According to the author, enargite could have acted as electron-donating electrode and dissolves (Eq. 11), whereas the activated carbon could have acted as electron-accepting electrode providing an extra surface area for the reduction of the oxidant agent (Eq. 12) resulting in an increase of the dissolution rate of enargite. A schematic representation of the described mechanism for enargite leaching in the presence of an activated carbon is presented in Figure 6.

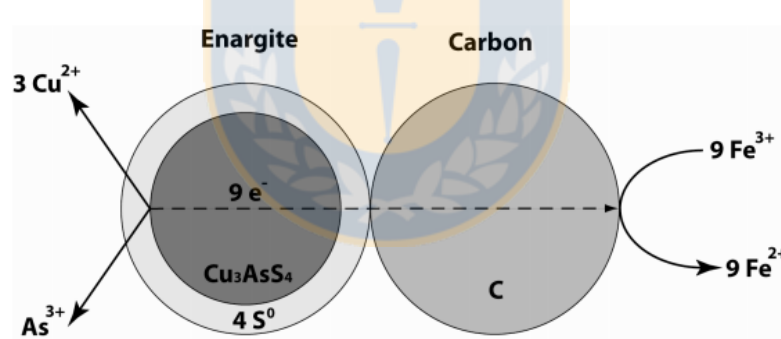
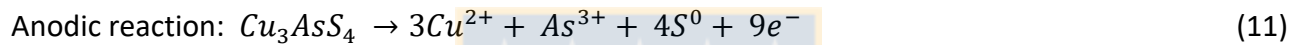


Figure 6. Schematic illustration of galvanic interactions between enargite and activated carbon particles. (Ghanad, 2011)

Ghanad (2011) and Dixon & Rivera-Vásquez (2012) also observed that recycled catalyst was approximately as effective as fresh activated carbon for enargite leaching up to three cycles can be seen in Figure 7. On the other hand, in the gold industry, it is reported that the activated carbon can be reused between 100 to 400 cycles of absorption and elution depending on the type of carbon and the reactivation process. (Marsden & House, 2006)

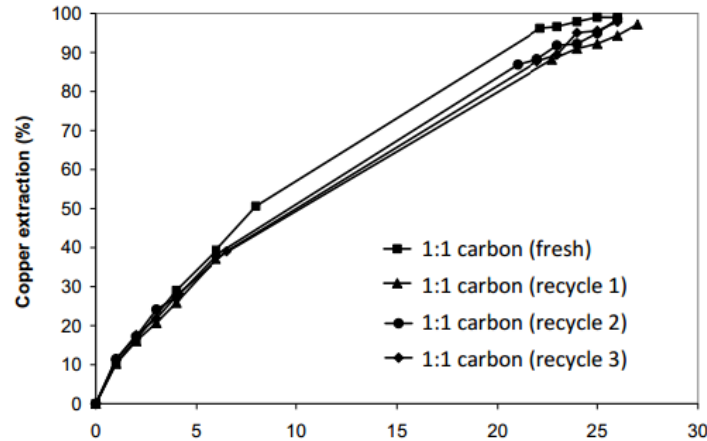


Figure 7. Effect of recycling activated carbon on copper extraction from enargite concentrate (Ghanad, 2011).

3.3.2 Possible hydrogen peroxide generation

Ahumada et al. (2002) noted that some of the activated carbon types can produce hydrogen peroxide (H_2O_2) in the presence of oxygen at acidic pH. On the activated carbon surface, ferrous oxidation can happen because of hydrogen peroxide generation. The authors outlined the oxidation of Fe(II) ions in the presence of activated carbon and oxygen as shown in Eq. 13 and 14., where C_{red}^* represents reduced carbon surface. Hydrogen peroxide generated in Eq. 13 is then used to oxidize Fe(II) ions as can be seen in Eq.14.



A new arsenic oxidation process was conducted by Choi et al. (2014), who used activated carbon to catalyze the oxidation reaction of arsenite to arsenate in the presence of oxygen as the only consumable reagent using acidic conditions at atmospheric pressure and temperature. The authors reported that the As(III) was oxidized to As(V) at 99% efficiency in less than 24 hours and they outlined that the catalytic effect of activated carbon is due to the in-situ formation of strong oxidant such as H_2O_2 . Choi and co-workers (2014) proposed a possible hypothesis where water and oxygen react on the activated carbon surface to produce hydrogen peroxide in accordance

with Eq. 15 and subsequently hydrogen peroxide will oxidize As(III) to form As(V) as shown in equation Eq. 16.



Ranzinski & Ghahremaninezhad (2015) and Ranzinski (2017) also investigated the mechanism of activated carbon catalyzed arsenic oxidation under the same condition of Choi et al. 2014. Ranzinski & Ghahremaninezhad (2015) and Ranzinski (2017) determined by ultra-violet visible spectrophotometry that hydrogen peroxide was formed in-situ and was still present at the end of the experiment. The authors suggested that there may be higher concentration of hydrogen peroxide in the solution but this concentration was decreased at the end of the test by the decomposition of hydrogen peroxide when it is in contact with solids. Radzinski (2017) reported that 16 g/L of H₂O₂ was detected in 100 mL of 1 mol/L sulfuric acid solution with 0.2 L/min oxygen sparging rate in the presence of 400 g of activated carbon after an hour.

Radzinski (2017) confirmed that the oxidation rate is dependent on the oxygen present in the system observing that the activated carbon in the absence of oxygen has a limited ability to produce hydrogen peroxide and thus it has a limited capacity to oxidize arsenic and therefore oxygen must be supplied into the system in order to enhance the process.

Radzinski (2017) pointed out that there two possible mechanisms may be occurring during the experiment and suggested that likely both of them are occurring at the same time. Both cases assume that there is hydrogen peroxide present in the system. The first hypothesized mechanism of arsenic oxidation is that As(III) is oxidized when it contacts with hydrogen peroxide and subsequently is adsorbed onto the activated carbon surface as As(V). The second reaction pathway is that As(III) is adsorbed onto the activated carbon surface and then is oxidized via hydrogen peroxide present in the close proximity of the surface of activated carbon to form As(V).

4. EXPERIMENTAL

An overall description of the experimental condition, materials, instrumentation and procedure methods used during this study are presented in this chapter. The study can be separated in two sections: (a) chalcopyrite and enargite leaching assisted by activated carbon considering the quantification and speciation of copper, iron and arsenic. (b) Contact tests between synthetic PLS and activated carbon.

4.1 Experimental condition

Because the principal aim of this study was to understand the effect of activated carbon on chalcopyrite and enargite leaching, the following experimental conditions have been chosen based in preliminary tests and considering other technical and theoretical information of previous research as described in Table 1. Contact tests between PLS and activated carbon follow similar conditions to leaching tests as can be seen in Table 2.

Table 1. Experimental conditions to determine the effect of activated carbon on chalcopyrite and enargite leaching.

Ratio activated carbon/concentrate	1
Concentrate (chalcopyrite or enargite)	50 g
Solution volume	1 L
Fe(III) (as FeCl ₃)	4 g/L
Cu(II) (as CuCl ₂)	4 g/L
HCl	0.5 M
NaCl	1.5 M
Temperature	90°C
O ₂ sparging	0.1 L/min
pH	< 0.5
Stirring speed	800 rpm
Leaching time	96 h

Table 2. Experimental conditions for contact tests between PLS and activated carbon at different conditions.

Activated carbon	5 g
Solution volume	100 mL
Fe(III) (as FeCl ₃)	5g/L
Cu(II) (as CuCl ₂)	5 g/L
As(III)	2 g/L
HCl	0.5 M
NaCl	1.0 M
Temperature	25°C, 80°C
O ₂ sparging	0, 0.1 L/min
pH	< 0.5
Stirring speed	800 rpm
Total time	360 min

4.2 Materials

Chalcopyrite and enargite flotation concentrate from an unknown mine were utilized as the test material in this work. All the reagents used for the preparation of solutions were analytical grade materials: sodium chloride, NaCl (Fisher chemical, 99%); hydrochloric acid, HCl (Sigma Aldric); hexahydrate ferric chloride, FeCl₃ (Sigma Aldrich, 98%) as a source of ferric ions and hydrated cupric chloride, CuCl₂ (Acros organics, 99%) as a source of cupric ions. The gas used in the experiments was industrial grade oxygen with minimum 99.5% purity and the activated carbon used for all experiments was derived from coconut shells with maximum ash content of 5% by weight which is typically used in the gold industry.

4.3 Sample preparation

4.3.1 Activated carbon preparation

For the leaching and contact tests, fresh activated carbon was pulverized for 5 s in a ring pulverizer. The pulverized activated carbon was dried for 15 minutes and then was sized in the range -120 +400 mesh (-125 +37 μm) in order to obtain sample of 50 g. The day before each experiment, activated carbon was wetted in deionized water overnight at 350 rpm. If the activated carbon was not wetted before the tests, activated carbon would absorb some solution volume and

therefore the solution would noticeably decrease over the duration of each test affecting their results.

4.3.2 Concentrates preparation

The mineral samples used in this study included a chalcopyrite concentrate and enargite concentrate from an unknown mine both corresponds to concentrates generated by flotation. The samples were prepared using a ring mill and then were classified into narrow size fractions with an average size distribution of 53 μm which corresponds to a 230 mesh.

4.4 Equipment

The leaching tests were performed in a 2 L sealed batch reactor equipped with a J-KEM scientific reactor controller, which could handle the temperature and also was fitted with an overhead stirrer, which allowed the mixing of the leach solution. Oxygen was provided during test through a gas sparger connected to a compressed gas cylinder. A reflux condenser was also fitted to the reactor lid preventing excessive evaporation of the solution. Figure 8 shows the set-up of the equipment used for the leaching tests.

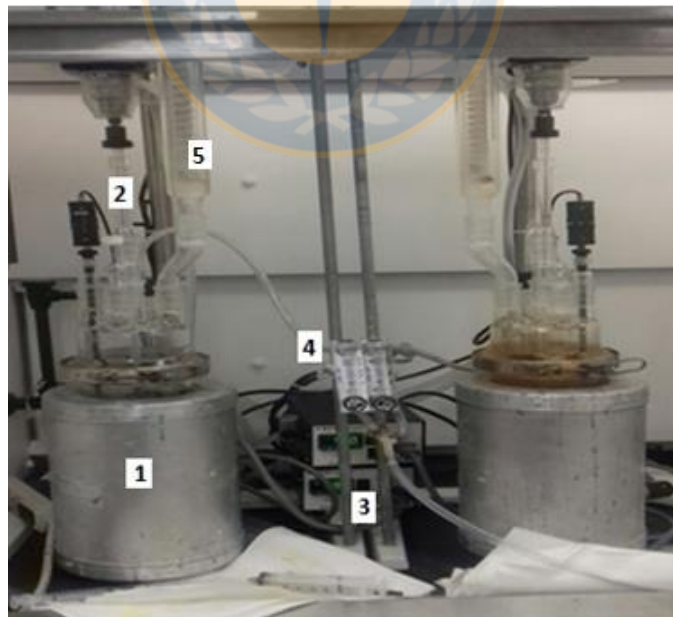


Figure 8. Leaching setup for the experiments.(1)Reactor; (2) Overhead stirrer; (3) J-KEM temperature controller; (4) Gas sparger; (5) Reflux condenser.

All the contact tests between PLS and AC were conducted in a 0.5 L glass jacketed sealed reactor with double glass walls connected to a water bath that controls the temperature of the whole experiment by re-circulating water. The reactor was equipped with a gas sparger connected to a compressed gas cylinder and the reactor was placed on a magnetic stirrer in order to allow the mixing of the solution. The experimental set-up can be seen in Figure 9.

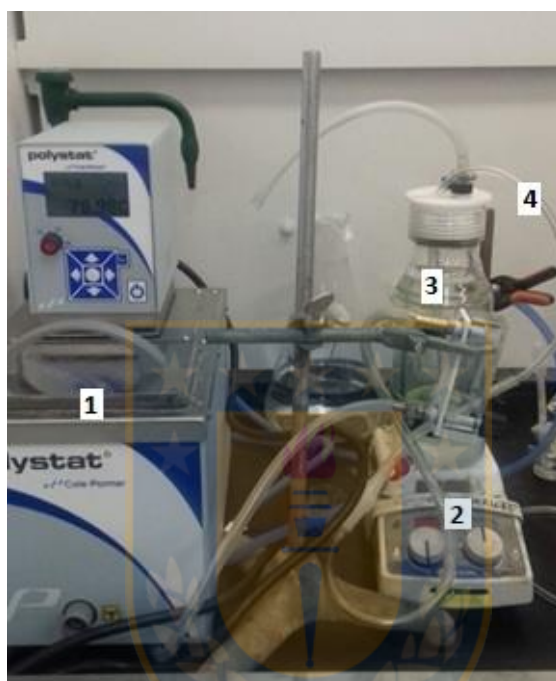


Figure 9. Set up for the batch-contact PLS – AC experiments. (1) Water bath; (2) Magnetic stirrer; (3) Glass jacketed reactor; (4) Gas sparger.

4.5 Experimental procedure

4.5.1 Leaching experimental procedure

Enargite and chalcopyrite leaching tests were carried under atmospheric pressure and constant pH approximately 0.5.

First, 1L of solution was prepared following the conditions described in table 1., thus, determined amount of sodium chloride, hydrochloric acid, hexahydrate ferric chloride, hydrated cupric chloride, and DI water were added to a beaker which was placed in a magnetic stirrer in order to guarantee the complete dissolution.

After that, the solution was transferred to the reactor. When the temperature of the solution reached 90°C, the experiment was initiated by adding the concentrate sample (enargite or chalcopyrite) and the activated carbon simultaneously in a ratio 1:1.

Finally, the reactor was connected to the oxygen flow provided by a compressed gas cylinder and the overhead stirrer. Samples about 15 mL each were withdrawn from the solution using syringe at 0,1, 3,6,12,24,36,48,60,72,84 and 96 h.

The samples were filtered using 0.45 μm syringe filters to separate the insoluble particles from the liquid phases. The filtrates were analyzed by an Agilent 4200 microwave plasma-atomic emission spectrometer (Figure 11) to measure the total concentration of copper, iron and arsenic and titration was performed to quantify the concentration of Fe(II), Cu(I) and As(III) ions subsequently the concentration of Fe(III), Cu(II) and As(V) was found by comparison with the total concentration of Fe, Cu and As.

Once the last sample was taken, the leach solution was filtered using a funnel and filter paper. The solid remaining in the filter paper was washed twice with a solution 10% of hydrochloric acid. Solid samples obtained were analyzed XRD.

4.5.2 Contact test experiment procedure

In all the contact experiments between PLS and activated carbon was used an initial solution with a concentration of 5/L Fe(III), 5/L Cu(II) and 2g/L As(III). Iron and copper were added in the form of ferric chloride and cupric chloride respectively. Arsenic (III) was prepared separately because of slow solubility and added to the initial solution.

The initial solution was prepared in a 100 mL glass beaker where the desired amount of sodium chloride, hydrochloric acid, ferric chloride, cupric chloride and 20 mL of premade 2g/L As (III) were added to the beaker and lastly DI water was added to complete the total volume of 100 mL as described in table 5.

The beaker was placed in a magnetic stirrer in order to ensure the complete dissolution of the reagents. Temperature was adjusted at 25°C and 80°C according to the requirement of each experiment. Once the reactor reached the desired temperature, the prepared solution was

transferred to 0.5L glass jacketed batch sealed reactor and then was immediately added the activated carbon.

Finally the reactor was sealed and connected with a compressed gas cylinder which supplied a flow rate of oxygen of 0.1 L/min into the system. The tests were also conducted at atmospheric pressure and constant pH less than 0.5 under stirrer speed of 800 rpm.

Solutions samples of 5 mL each were taken from the solution using a syringe at 0, 5, 20, 60, 200, 300 and 360 min. Then the samples were filtered using 0.45 μm syringe filters to separate the insoluble particles from the liquid phases. Finally, the filtered solutions were analyzed by an Agilent 4200 microwave plasma-atomic emission spectrometer (Figure 10) to measure the total concentration of copper, iron and arsenic. Titration was utilized to measure the concentration of Fe(II), Cu(I) and As(III) and subsequently the concentration of Fe(III), Cu(II) and As(V) was found by comparison with the total concentration of Fe, Cu and As.

For the nitric acid treated activated carbon a 0.5 M solution of nitric acid was used which was mixed with the activated carbon for 24 hours. Finally the activated carbon was washed 3 times with DI water before its use.



Figure 10. Agilent 4200 MP-AES microwave plasma-atomic emission spectrometer used to analyze liquid samples.

5. RESULTS AND DISCUSSION

5.1 Mineralogical composition of samples

The mineralogical composition of chalcopyrite concentrate and enargite concentrates used in this study were determined using quantitative X-ray powder diffraction (XRD) and the results are presented in Table 3 and Table 4 respectively.

Table 3. XRD analysis of the chalcopyrite concentrate sample

Mineral	Chemical formula	%wt
Chalcopyrite	CuFeS_2	66.1
Pyrite	FeS_2	12.1
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	16.4
Gypsum	$\text{CaSO}_4 \cdot \text{H}_2\text{O}$	0.5
Muscovite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	2.4
Annite (Fe-biotite)	$\text{KFe}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	2
Kaolinite	$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$	0.5
Total		100

Table 4. XRD analysis of the enargite concentrate sample

Mineral	Chemical formula	%wt
Enargite	Cu_3AsS_4	45.5
Pyrite	FeS_2	28.3
Chalcopyrite	CuFeS_2	4.1
Chalcocite	Cu_2S	3.9
Quarz	SiO_2	18.2
Total		100

5.2 Effect of activated carbon addition on sulfide leaching

The effect of activated carbon on chalcopyrite and enargite leaching in chloride media can be seen in Figure 11 and 12 when the activated carbon/concentrate ratio in both leaching experiments was 1. The graphics show that chalcopyrite and enargite leaching at 90°C was significantly enhanced by the addition of activated carbon.

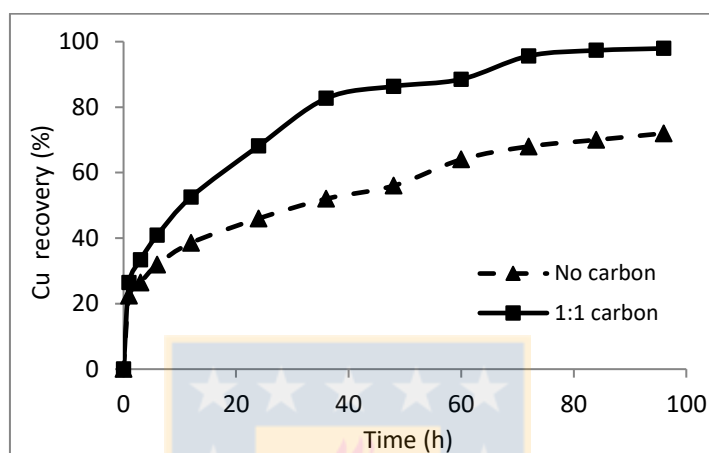


Figure 11. Effect of AC on chalcopyrite leaching in chloride media at 90°C. Initial condition: 1.5 M Cl⁻, 4 g/L Cu(II), 4 g/L Fe(III) in 1 L solution, conc./AC = 1:1 and oxygen flow rate = 0.1 L/min.

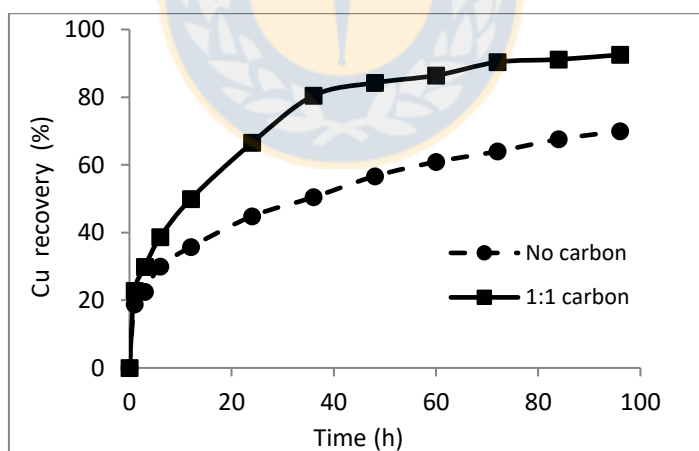


Figure 12. Effect of AC on enargite leaching in chloride media at 90°C. Initial condition: 1.5 M Cl⁻, 4 g/L Cu(II), 4 g/L Fe(III) in 1 L solution, conc./AC = 1:1 and oxygen flow rate = 0.1 L/min.

The catalyst addition increased the copper recovery on chalcopyrite leaching from approximately 72% to 97% within 96 hours. A similar effect was observed during the enargite leaching where the increase in the copper recovery was nearly from 70% to 92% over the same

leaching time. The mechanism of the catalytic effect of activated carbon is not completely understood yet, but it is believed that the mechanism behind this catalytic effect is linked to the surface chemistry of the catalyst.

Some types of activated carbon are able to generate hydrogen peroxide in the presence of oxygen through the functional groups on its surface which can cause oxidation in the aqueous media (Ahumada et al, 2002; Choi et al., 2014; Radzinski & Ghahremaninezhad, 2015; Radzinski, 2017). In this sense, the effect of activated carbon on sulfide leaching could be attributed to the formation of hydrogen peroxide on the activated carbon surface during leaching of chalcopyrite and enargite. Hydrogen peroxide is a strong oxidant; therefore it can maintain proper oxidizing conditions during leaching. From the literature it is well known that hydrogen peroxide has proven to be an effective oxidant in different research however its use is very limited due to its high cost. For this reason, it could be very advantageous for a process to produce hydrogen peroxide in-situ. The details of the hydrogen peroxide quantification and its oxidation mechanism in both chalcopyrite and enargite leaching are still being investigated by the hydrometallurgy group at Queen's University.

On the other hand, another possible explanation for the results obtained in leaching in the presence of activated carbon in both chalcopyrite and enargite is through a possible galvanic interaction between activated carbon and the sulfide mineral as reported by Nakazawa et al. (1998), Zhang & Gu (2007), Liang et al. (2010), and Ghanad, (2011). The effect of activated carbon on sulfide leaching requires further work to develop a more detailed understanding with respect to the present hypotheses.

5.3 Recovery of Cu, Fe and As in the leaching experiment in the present of activated carbon

The recovery of copper and iron for the chalcopyrite concentrate leaching test and the recovery of copper, iron and arsenic for the enargite concentrate leaching are presented in Figure 13 and 14, respectively. In Figures 13 and 14 it can be seen that copper recovery in both chalcopyrite and enargite leaching followed similar trends which is in agreement with the literature. However, the recovery of copper in chalcopyrite leaching is slightly higher, then recoveries of 97% were obtained for chalcopyrite concentrate leaching and 92% for enargite concentrate leaching in the presence of activated carbon.

On the other hand, iron recovery did not follow the same trend in both leaching experiments showing a completely different behavior. The recovery of iron from the chalcopyrite concentrate began following a trend similar to that of the copper during the first 12 hours of the experiment. After that, it can be seen from Figure 13 that the concentration of iron declined to the end of the experiment due to the precipitation of iron by the formation of jarosite in the solution, which was verified by XRD analysis.

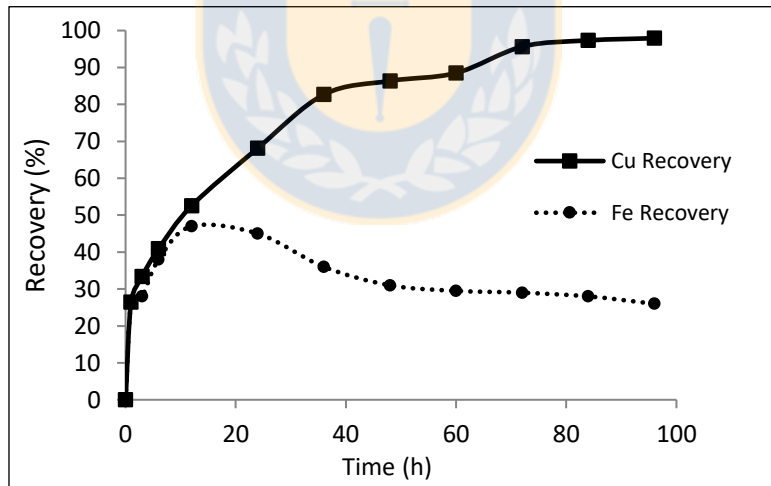


Figure 13. Recovery of Cu and Fe on chalcopyrite concentrate leaching in the presence of AC at 90°C. Initial condition: 1.5 M Cl^- , 4 g/L Cu(II), 4 g/L Fe(III) in 1 L solution, conc./AC = 1:1 and oxygen flow rate = 0.1 L/min.

The recovery of iron from enargite concentrate followed a linear trend until it reached the point of precipitation after 84 hours of leaching as shown in Figure 14. Arsenic recovery increased over the time until its co-precipitation with the iron in the form of scorodite which also was

verified by XRD analysis. In the enargite leaching experiment, pyrite was the source of the dissolved iron, which represented 28.3% in the enargite concentrate (Table 4).

Partial pyrite dissolution was observed in the leaching experiments of both enargite and chalcopyrite. Nevertheless iron dissolution from pyrite should not have occurred according to the literature in chloride media in both enargite and chalcopyrite where all previous studies reported that pyrite remained unreacted in the leaching system. Under the presence of activated carbon in the leach solution, the pyrite oxidation could have been catalyzed being a source of iron in the solution.

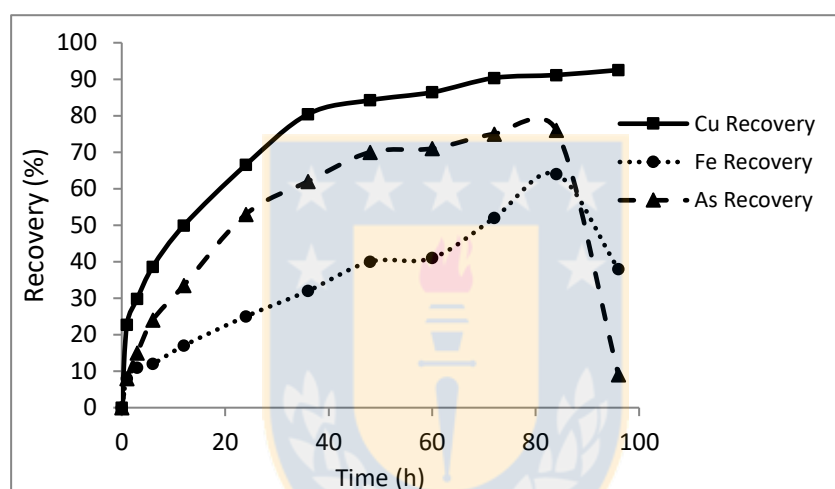


Figure 14. Recovery of Cu, Fe and As on enargite concentrate leaching in the presence of AC at 90°C. Initial condition: 1.5 M Cl⁻, 4 g/L Cu(II), 4 g/L Fe(III) in 1 L solution, conc./AC = 1:1 and oxygen flow rate = 0.1 L/min.

5.4 Speciation of Copper, Iron and Arsenic in the leaching experiments in the present of AC

5.4.1 Iron speciation in the leaching experiment

The concentrations of ferric and ferrous ions are depicted in Figure 15 for chalcopyrite concentrate leaching and in Figure 16 for the enargite concentrate leaching experiment. When activated carbon was added to the leaching reactors about 3g/L of ferric were reduced to ferrous ions in both chalcopyrite and enargite leaching tests in the first hour.

After the first hours, the concentration of ferrous ions continuously declined in both cases. In the chalcopyrite leaching (Figure 15), the concentration of Fe(II) ions decreased from 5.0 g/L to 2g/L while the concentration of Fe(III) ions declined slightly due to jarosite precipitation. The decrease of Fe (II) ions could have been due to the catalytic effect of activated carbon, which could be explained by the hypothetical hydrogen peroxide formation.

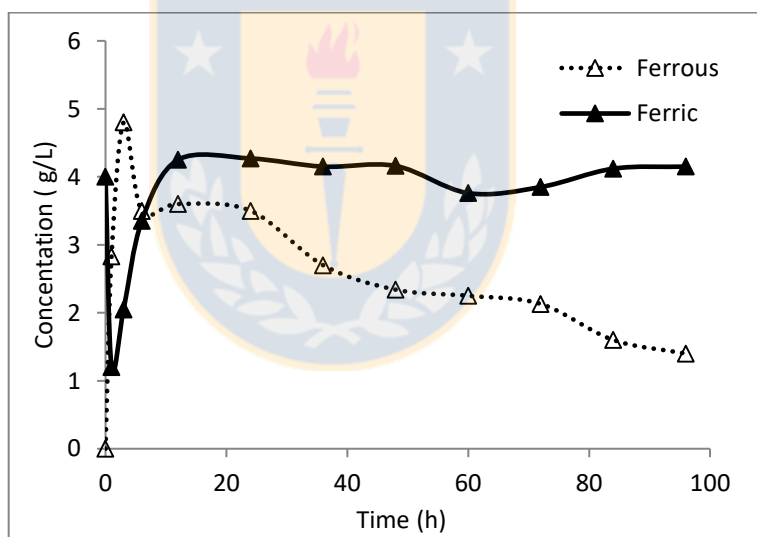


Figure 15. Ferric and ferrous concentration in chalcopyrite leaching experiment at 90°C. Initial condition: 1.5 M Cl⁻, 4 g/L Cu(II), 4 g/L Fe(III) in 1 L solution conc./AC = 1:1 and oxygen flow rate = 0.1 L/min.

On the other hand, in the case of enargite leaching experiment (Figure 16), the concentration of ferrous ions decreased from 3 g/L to 1.5 g/L, while the concentration of ferric ions increased until the precipitation began when the concentration of ferric was approximately 5.2 g/L. Finally the

concentration of ferric ions declined product of co-precipitation with arsenic as a scorodite and the concentration of ferrous remained constant.

This behavior may be explained considering that at first, the decrease of ferric ions was due to the presence of oxygen functional groups on the surface of the activated carbon which reduced ferric ions (Figueiredo et al., 2006). After that, activated carbon apparently facilitated oxidation of ferrous ions increasing the concentration of ferric ions through the possible generation of hydrogen peroxide (Radzinski 2017).

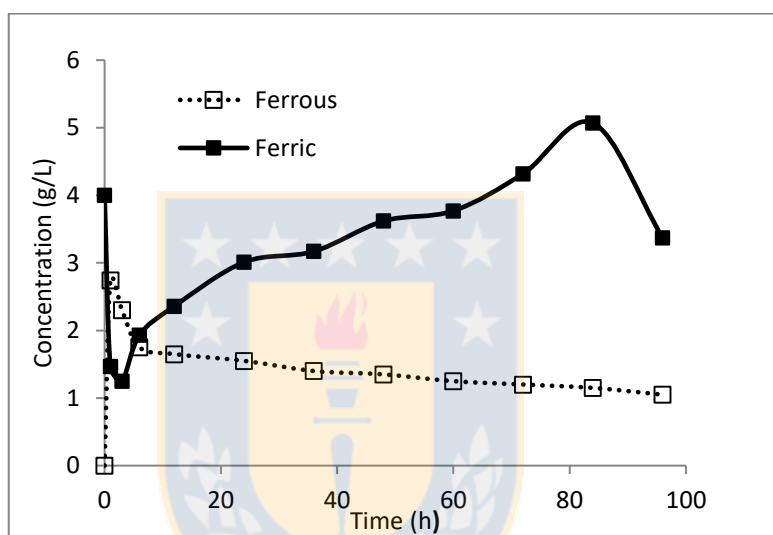


Figure 16. Ferric and ferrous concentration in the enargite leaching experiment at 90°C. Initial condition: 1.5 M Cl⁻, 4 g/L Cu(II), 4 g/L Fe(III) in 1 L solution, conc./AC = 1:1 and oxygen flow rate = 0.1 L/min.

5.4.2 Copper speciation in leaching experiment

The concentrations of cupric and cuprous ions are plotted in Figure 17 for chalcopyrite leaching and in Figure 18 for the enargite leaching experiment which followed a similar behavior.

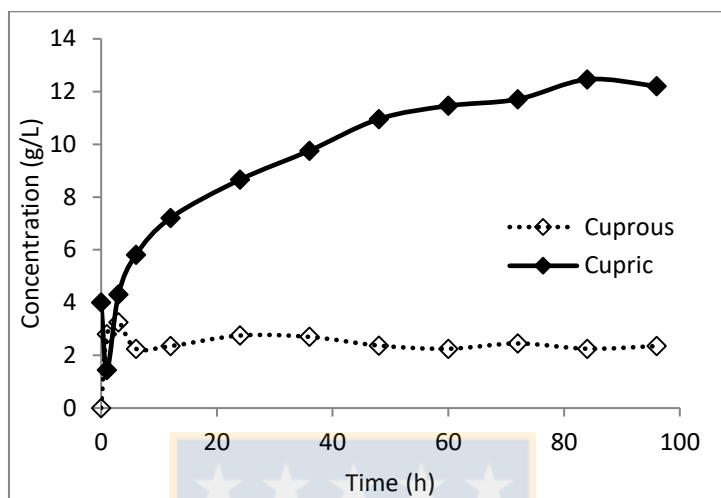


Figure 17. Cupric and cuprous concentration in the chalcopyrite leaching experiment at 90°C. Initial condition: 1.5 M Cl^- , 4 g/L Cu(II), 4 g/L Fe(III) in 1 L solution, conc./AC = 1:1 and oxygen flow rate = 0.1 L/min.

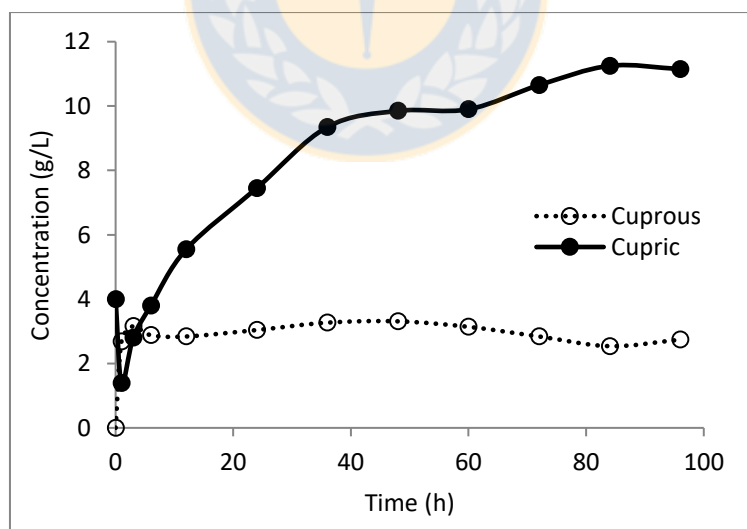


Figure 18. Cupric and cuprous concentration in the enargite leaching experiment 90°C. Initial condition: 1.5 M Cl^- , 4 g/L Cu(II), 4 g/L Fe(III) in 1 L solution, conc./AC = 1:1 and oxygen flow rate = 0.1 L/min.

In both enargite and chalcopyrite leach solution, when activated carbon was added about 3g/L of cupric were reduced to cuprous during the first hour. After that, the concentration of Cu(I) ions remained constant and the majority of the remaining copper was found as Cu(II) in both solutions which increased throughout the experiment. The justification of how activated carbon acted on Cu(II) ions is appears to be similar to its effect on Fe(III) ions as explained in the above section.

5.4.3 Arsenic speciation in leaching experiment

The concentrations of arsenite and arsenate ions on the enargite leaching experiment are shown in Figure 19. It can be seen that most of the arsenic present in the solution is present as arsenate, which is coherent with the reactions described in the literature (Padilla et al., 2005). The analysis of the leach solution showed that the concentration of As(III) decreased during the experiment and that only a small amounts of concentration below 120 ppm were observed. After the 36th hours of the test no concentration of As(III) was detected which means that the entire arsenic content was in the form of As(V) ions. After 84 h, the concentration of As(V) decreased significantly due to precipitation as a scorodite.

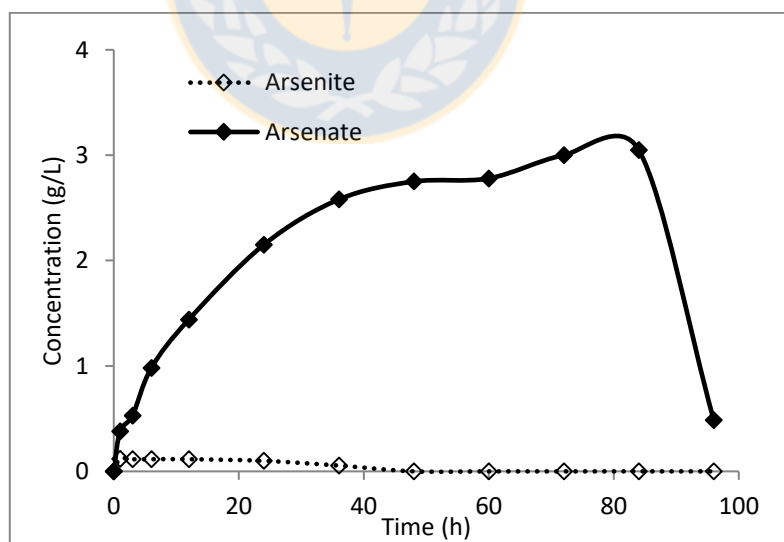


Figure 19. Arsenite and arsenate concentration in enargite leaching experiment at 90°C. Initial condition: 1.5 M Cl⁻, 4 g/L Cu(II), 4 g/L Fe(III) in 1 L solution conc./AC = 1:1 and oxygen flow rate = 0.1 L/min.

5.5 Contact tests between PLS and activated carbon

Four different set of contact tests were carried out in the presence of activated carbon and PLS varying the initial conditions such as temperature, oxygen flow rate and the pretreatment of activated carbon with nitric acid in order to prove the reduction and oxidation behavior of ions and the adsorption of these in activated carbon. The initial concentration for Cu(II) and Fe(III) was 5 g/L for each ion and 2 g/L for As(III) in 100 mL solution mixed with 5 g of activated carbon in all tests

Condition 2 in Figures 20 to 27 was used as a reference since it simulates the same conditions of the chalcopyrite and enargite leaching experiments in term of temperature, oxygen and type of carbon.

5.5.1 Adsorption of copper, iron and arsenic by activated carbon

Activated carbon has a large surface area which along with its physical properties causes the adsorption of ions on its surface. Four series of experiments were performed to prove the adsorption properties of activated carbon for iron, arsenic and copper. Figures 20, 21 and 22 describe the adsorption efficiency of iron, copper and arsenic with respect to the initial concentration of each ion onto the activated carbon surface as a function of time.

The initial absorption for iron, copper and arsenic onto activated carbon were rapid at the beginning and then plateaued starting at approximately at 60 min. In this sets of tests no adsorption was measured later than the first 60 min of experiment. In accordance to Figures 21 and 22, it was found at the end of the experiment that an average amount of 16% and 20% of copper and iron were absorbed in the activated carbon respectively, which means that approximately 84% of the total copper and 80% of total iron remained in solution probably as chloro-complex ions in its majority. However, there is uncertainty if as time goes, desorption may occur since in the leaching tests the absorption effect had an apparently irrelevant effect due to the high copper recoveries obtained as are depicted in Figures 11 and 12.

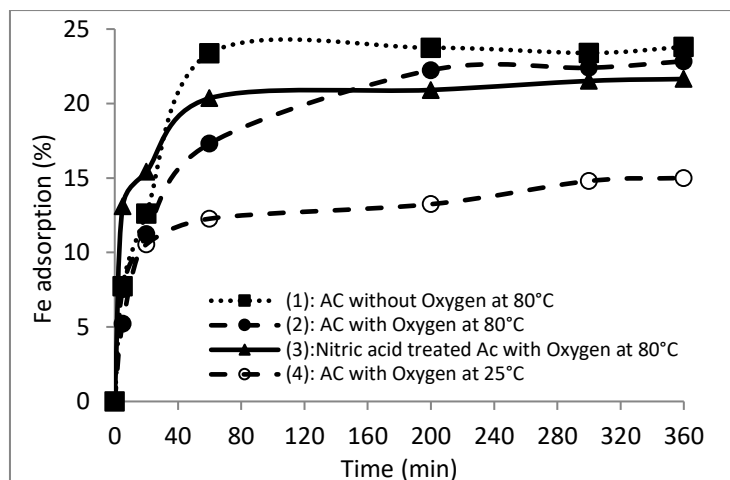


Figure 20. Efficiency of iron adsorption onto activated carbon versus time. Initial conditions: 0.5M HCl-1M NaCl 100 mL solution ($\text{Fe}^{3+} = 5 \text{ g/L}$, $\text{Cu}^{2+} = 5 \text{ g/L}$, $\text{As}^{3+} = 2 \text{ g/L}$ and AC = 5 g).

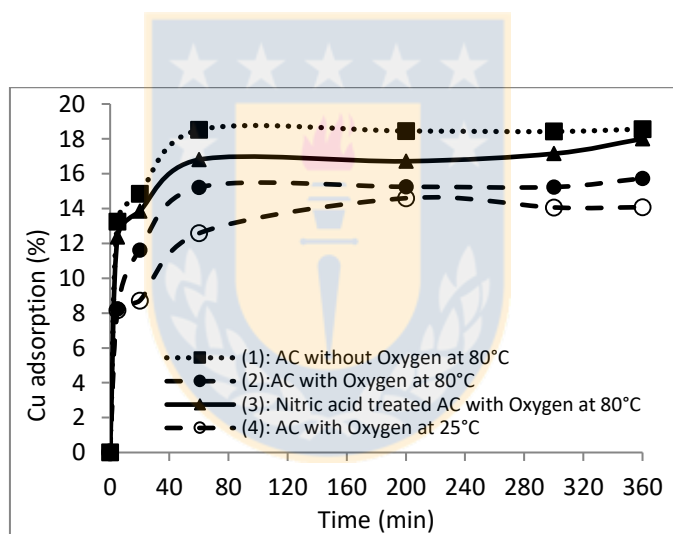


Figure 21. Efficiency of copper adsorption onto activated carbon versus time. Initial conditions: 0.5M HCl-1M NaCl 100 mL solution ($\text{Fe}^{3+} = 5 \text{ g/L}$, $\text{Cu}^{2+} = 5 \text{ g/L}$, $\text{As}^{3+} = 2 \text{ g/L}$ and AC = 5 g).

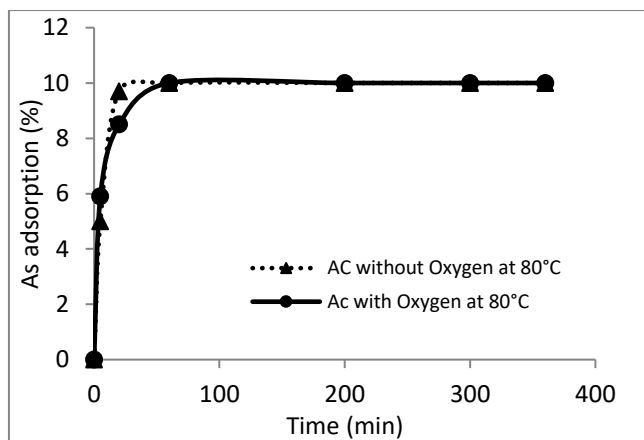


Figure 22. Efficiency of arsenic adsorption onto activated carbon versus time. Initial conditions: 0.5M HCl-1M NaCl 100 mL solution ($\text{Fe}^{3+} = 5 \text{ g/L}$, $\text{Cu}^{2+} = 5 \text{ g/L}$, $\text{As}^{3+} = 2 \text{ g/L}$ and AC = 5 g).

In general, the curves show the same adsorption behavior for both copper and iron, although in both situations where room temperature was used (curve 4), lower absorption was achieved which is attributed to a kinetic effect, since at lower temperature is accomplished lower ionic mobility which subsequently could cause that the ions are moved more slowly towards the micropores of the activated carbon. The arsenic absorption for all evaluated conditions (Figure 23) was approximately 10% which means that 200 mg/L of the available 2g/L arsenic in the initial solution was adsorbed onto the activated carbon surface (Figure 22)

It is important to highlight that the use of activated carbon could represent an important advantage for a process in spite of absorption of ions because it is easy to release the adsorbed ions from activated carbon, applying a washing step that allows their potential reuse as happens in the gold industry (Marsden & House, 2006).

5.5.2 Reduction and oxidation behavior of ions in solution in the presence of activated carbon

From the literature it is reported that the catalytic effect of activated carbon can cause hydrogen peroxide generation and subsequent oxidation could help the leaching process. Four experiments were carried out at different conditions in order to prove the reduction and oxidation behavior of ions present in the synthetic PLS

5.5.2. Copper behavior in the solution

Figures 23 and 24 show the cupric and cuprous ion concentration in solution in the presence of activated carbon versus time at different conditions. In accordance to Figures 23 and 24, the initial concentration of Cu(II) ions initially decreased because parts of these ions were immediately reduced and also were adsorbed when they came into contact with the surface of the activated carbon. Then the concentration of Cu(II) ions increased as a product of oxidation of Cu(I) to Cu(II) ions when oxygen was supplied in the experiment. An increase in Cu(II) concentration was not pronounced in the case that oxygen was not added into the system (curve 1) as the other conditions.

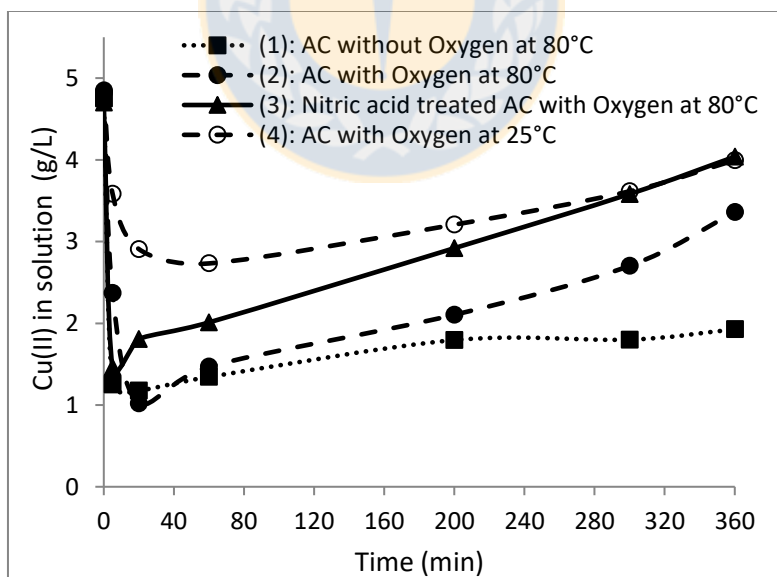


Figure 23. Concentration of cupric ions in the solution versus time in the presence of AC. Initial conditions: 0.5M HCl-1M NaCl 100 mL solution ($\text{Fe}^{3+} = 5 \text{ g/L}$, $\text{Cu}^{2+} = 5 \text{ g/L}$, $\text{As}^{3+} = 2 \text{ g/L}$ and AC = 5 g).

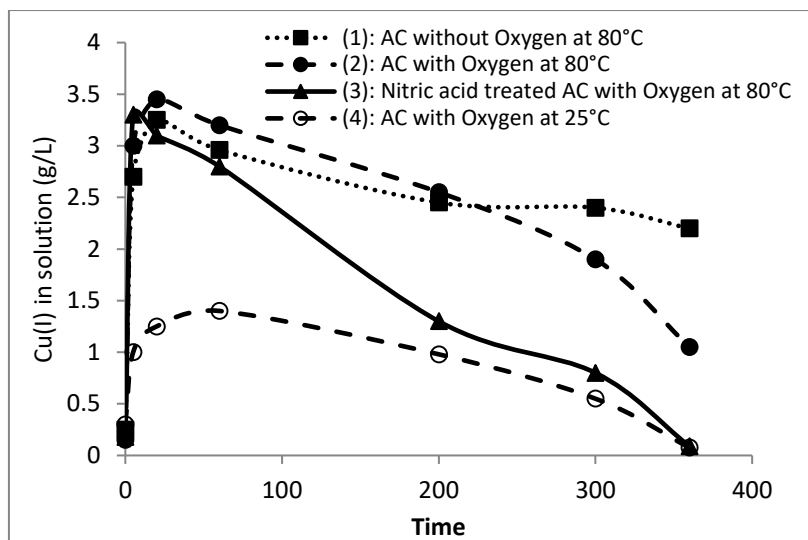


Figure 24. Concentration of cuprous ions in the solution versus time in the presence of AC. Initial conditions: 0.5M HCl-1M NaCl 100 mL solution ($\text{Fe}^{3+} = 5 \text{ g/L}$, $\text{Cu}^{2+} = 5 \text{ g/L}$, $\text{As}^{3+} = 2 \text{ g/L}$ and AC = 5 g).

The initial reduction of Cu(II) to Cu(I) ions could be explained by the presence of functional groups on the surface of the activated carbon. When oxygen was sparged through the experiments, it is likely that it has generated hydrogen peroxide which oxidized Cu(I) to Cu(II) consequently increasing the concentration of Cu(II) ions. The decrease in the concentration of cupric and cuprous is also influenced by the adsorption of these in the activated carbon as is depicted in Figure 21.

The lowest reduction value for the copper is related to the test with AC at 25°C (curve 4). For curve (1), it is verified that the non-injection of oxygen implies that oxidation of Cu(I) to Cu(II) is very limited. In accordance with Randzinski (2017) this condition will have a limited capacity to produce hydrogen peroxide into the system, which hypothetically will influence in the Cu(II) ion behavior. When comparing curves (2) and (4), it is appears that the lower temperature works better because the dissolved oxygen concentrate is hypothetically higher in this condition allowing a more favorable thermodynamic condition than higher temperature (curve 2), however lower temperature could not be kinetically adequate for sulfide leaching.

The difference in behavior between curve (2) and (3) at 80°C is due to the chemical pretreatment on activated carbon by means of nitric acid which caused changes in surface by

modifying its catalytic and adsorbent behavior associated to the modifications of the functional groups on its surface as reported by Figueiredo et al. (2006).

5.5.2.2 Iron behavior in the solution

The concentration of ferric and ferrous ions in the presence of activated carbon versus time is presented in Figures 25 and 26. According to Figures 25 and 26, part of the initial concentration of Fe(III) ions were rapidly reduced after the addition of activated carbon during the first minutes.

The reduction of Fe(III) ions proceeded near to completion if oxygen was not supplied into the system (curve 1) which means that all Fe(III) ions were reduced to Fe(II) ions, condition that could be unfavorable for sulfide leaching since Fe(II) ions are not strong oxidants in comparison to Fe(III) ions. In the case that oxygen was sparged through the reactor, oxidation of Fe(II) was observed in the system increasing the concentration of Fe(III) ions.

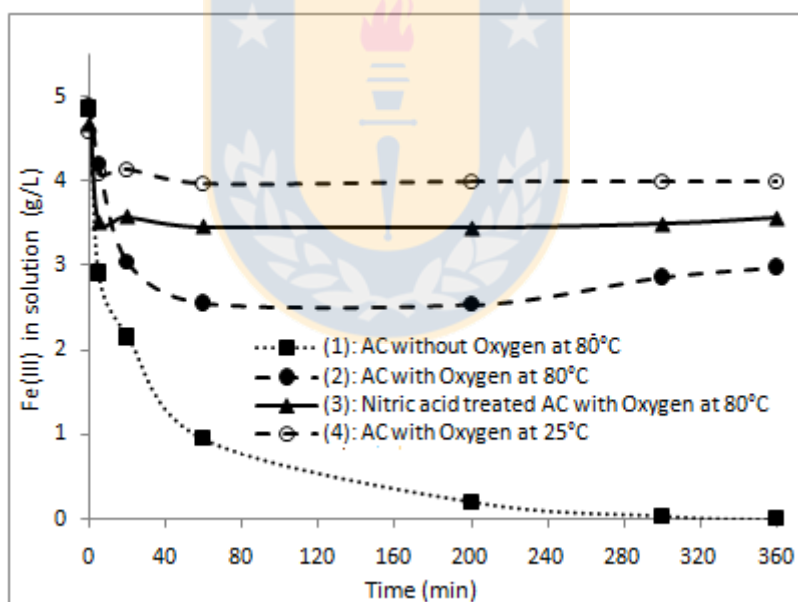


Figure 25. Concentration of Ferric ions in the solution versus time in the presence of AC. Initial conditions: 0.5M HCl-1M NaCl 100 mL solution ($\text{Fe}^{3+} = 5 \text{ g/L}$, $\text{Cu}^{2+} = 5 \text{ g/L}$, $\text{As}^{3+} = 2 \text{ g/L}$ and AC = 5 g).

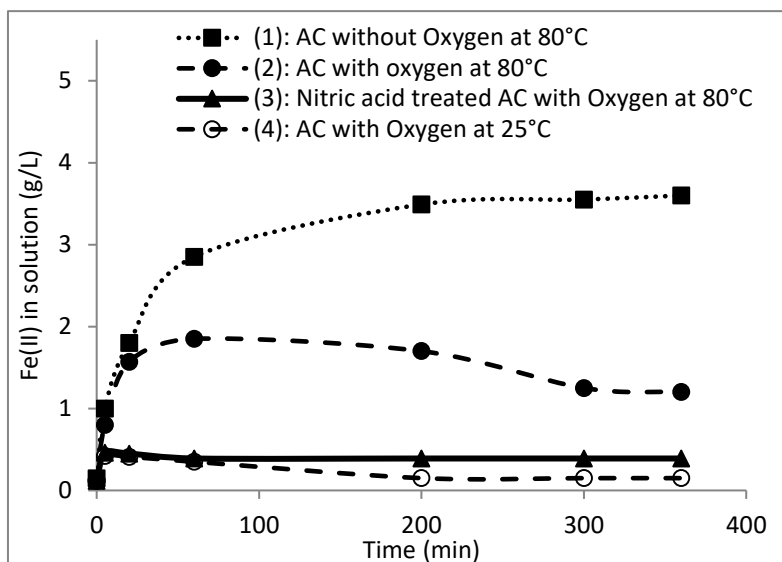


Figura 26. Concentration of Ferrous ions in the solution versus time in the presence of AC. Initial conditions: 0.5M HCl-1M NaCl 100 mL solution ($\text{Fe}^{3+} = 5 \text{ g/L}$, $\text{Cu}^{2+} = 5 \text{ g/L}$, $\text{As}^{3+} = 2 \text{ g/L}$ and AC = 5 g).

From curves (2) and (4), it can be observed that temperature has a great influence and this could be due to the higher solubility of oxygen at a lower temperature generating better thermodynamic condition as explained in the copper case. The decrease of Fe(III) ions was minimum in two cases: when nitric acid pretreatment was made on the catalyst (curve 3) and when room temperature was used (curve 4). It appears that Fe(III) ions are rapidly being consumed and regenerated in the solution and therefore the amount of Fe(III) ions can be maintained relatively high and constant in the solution as long as oxygen is injected.

To summarize the oxidation experiments generally confirmed that Fe(III) ions were initially reduced to Fe(II) ions apparently due to the presence of oxygen functional groups on the surface of catalysts. When oxygen was sparged through the experiments, this hypothetically reacted on the activated carbon surface generating hydrogen peroxide which oxidized Fe(II) ions increasing the concentration of Fe(III). The decrease in the concentration of ions is also influenced by the adsorption of these in the activated carbon as is depicted in Figure 20

5.5.2.3 Arsenic behavior in the solution

The effect of the catalyst on arsenic ions oxidation was studied in two situations in order to analyze the influence of the presence of oxygen and it is illustrated in Figure 27. From the results it can be seen that the oxidation of As(III) to As(v) occurred in the presence and in the absence of oxygen. With the non-addition of oxygen more than 50% of As (III) was oxidized to As(v) with activated carbon at 80 ° C. When oxygen is supplied in the reactor, As(III) oxidation proceeded to completion in about 6 hours. In this sense, oxygen is a key factor to obtain a rapid oxidation of all ions in the presence of activated carbon since the oxidation rate decreased considerably without the addition of oxygen.

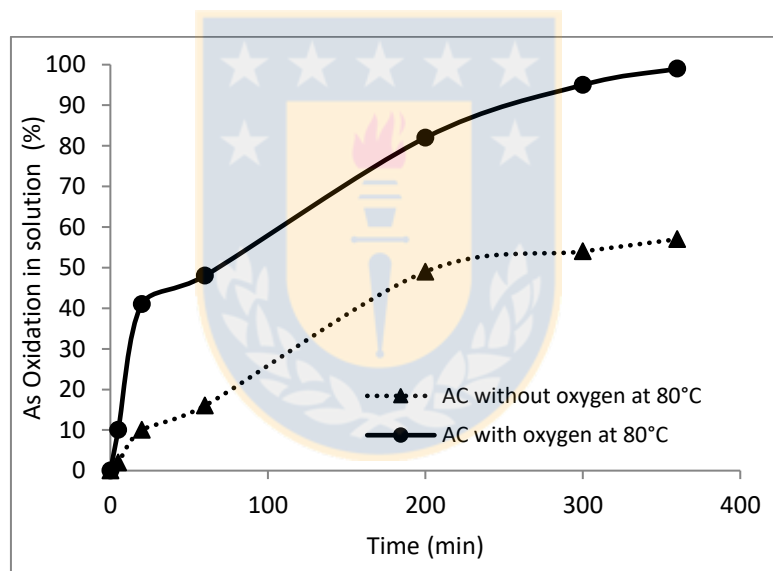


Figure 27. As oxidation (As(III) to As(V)) versus time in the presence of AC in chloride media. Initial conditions: 0.5M HCl-1M NaCl 100 mL solution ($\text{Fe}^{3+} = 5 \text{ g/L}$, $\text{Cu}^{2+} = 5 \text{ g/L}$, $\text{As}^{3+} = 2 \text{ g/L}$ and AC = 5 g).

The results are in agreement with Radzinski (2017), who reported that in the absence of oxygen, the catalyst can generate limited hydrogen peroxide and therefore oxidize a considerable minor amount of As(III). The oxidation of As (III) to As (V) is one of the most important advantages using carbon for arsenic bearing copper sulfide minerals leaching due to mainly environmental reasons.

6. CONCLUSIONS

The most important finding in this research was that the addition of activated carbon can significantly enhance both chalcopyrite and enargite leaching in chloride media under the condition tested copper recovery increased from 72% to 97% in chalcopyrite leaching and from 70% to 92% in enargite leaching within 96 hours.

The iron dissolution for chalcopyrite concentrate leaching started at the same rate as copper but precipitation of jarosite happened when the concentration of ferric ions reached 4.5 g/L. In the enargite leaching, precipitation of scorodite happened after 84 hours when the concentration of ferric and arsenate ions was 5 g/L and 3 g/L respectively, which was verified by XRD.

The speciation results of leaching suggest that when the carbon came in contact with the initial leach solution, the catalyst immediately reduced part of cupric and ferric ions to cuprous and ferrous ions seemingly by the presence of functional groups on its surface. Afterward carbon apparently helped to generate optimal condition that oxidize ferrous, cuprous and arsenite ions suggesting that catalyst behavior improved the leaching results.

According to the PLS – activated carbon contact tests, it is verified that the behavior of the ions in the leaching tests was influenced by the presence of the activated carbon. Activated carbon was strongly affected by the presence of oxygen, temperature and previous treatment on the surface catalyst. Results also suggested that the carbon pretreated with nitric acid could be a good condition for a leaching test since this carbon had one of the best oxidation behavior maintaining higher concentration of ferric and cupric ions.

Comparing the speciation results in the enargite and chalcopyrite leaching with condition 2 of the PLS – AC contact test (condition with same parameters as leaching), it is verified that the Cu, Fe and As follow similar trends in their reduction and oxidation behavior.

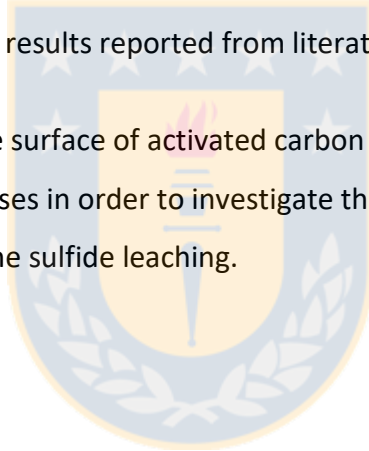
In the PLS - AC contact tests it was determined that there was partial absorption of Cu, Fe and As by the AC, however the absorption effect was apparently irrelevant in both enargite and chalcopyrite leaching due to its high copper recoveries. Therefore the observations were not coincident, which could suggest that desorption may occur during the course of the experiments.

7. RECOMMENDATIONS FOR FUTURE WORK

A possible line of work to continue and complete this study could be to consider the analysis of absorption and/or desorption of ions both in chalcopyrite and enargite leaching test together with a detailed analysis of activated carbon after its use in the leaching tests since there is uncertainty about how the absorption and/or desorption may or may not affect the leaching process principally because the results of adsorption in contact tests are not in accordance with the results of leaching tests.

Given the positive effect of activated carbon treated with nitric acid, another possible step for this research is to perform leaching using that type of carbon and compare the results with those obtained in this study. Additionally it is suggested to run tests using fresh and reused activated carbon due the positive results reported from literature.

Deepen the study about the surface of activated carbon and the functional groups formed during different activation processes in order to investigate the process behind it and analyze the implications that could have on the sulfide leaching.



8. REFERENCES

- Ahumada, E.**, Lizama, H., Orellana, F., Suárez, C., Huidobro, A., (2002). Catalytic oxidation of Fe (II) by activated carbon in the presence of oxygen. *Carbon*, 40(15), 2827-2834.
- Aroca, F.**, Backit, A., & Jacob, J. (2012). CuproChlor®, a hydrometallurgical technology for sulphides leaching. In *HydroProcess 2012* (pp. 97-108).
- Bonan, M.**, Demarthe, J. M., Renon, H., & Baratin, F. (1981). Chalcopyrite leaching by CuCl_2 in strong NaCl solutions. *Metallurgical and Materials transactions B*, 12(2), 269-274.
- Choi, Y.**, Ghahremaninezhad, A., & Ahern, N. (2014). Process for activated carbon-assisted oxidation of arsenic species in process solutions and waste waters. COM 2014 - Conference of Metallurgists.
- Dixon, D.G.**, Mayne, D.D., and Baxter, K.G., (2008). Galvanox –A novel galvanically-assisted atmospheric leaching technology for copper concentrates. *Canadian Metallurgical Quarterly*.
- Dixon, D.G.**, and Rivera-Vasquez, B., (2009). Leaching process for copper concentrates containing arsenic and antimony compounds”, International Patent WO 2009/135291.
- Dixon, D. G.**, & Rivera-vasquez, B. (2012). Leaching process for copper concentrates with a carbon catalyst. US.
- Dutrizac J.E.** (1981) The dissolution of chalcopyrite of ferric sulfate and ferric chloride media, *metallurgical transactions B*, vol 12B: 371-378.
- Dutrizac J. E.** (1990) Elemental sulphur formation during the ferric chloride leaching of chalcopyrite, *Hydrometallurgy*, 23: 153-176.
- Dutrizac J.E.** (1992) the leaching of sulphide minerals in chloride media, *Hydrometallurgy*, 29: 1- 45
- Figueiredo, J.**, Pereira, M. F., Freitas, M. M., Órfão, J. J., Jansen, R. J. J., van Bekkum, H., (2006). Activated carbon surfaces in environmental remediation. *Interface Science and Technology*.
- Ghanad I.G.** (2011). Atmospheric leaching of enargite in iron sulfate solutions catalyzed by activated carbon. MSc thesis, University of British Columbia, Canada.

- Havlik, T.** (2008). Hydrometallurgy Principles and applications, Woodhead Publ. Ltd., Cambridge (p. 536).
- Herreros O.,** Quiroz R., Hernandez M.C., &Viñals J. (2002). Dissolution kinetics of enargite in dilute Cl₂ / Cl⁻ media. Science, vol. 64, pp. 153–160.
- Hirato, T.,** Majima, H. &Awakura, Y. (1987) The leaching of chalcopyrite with cupric chloride, Metallurgical transactions B, vol 18B: 31-39.
- Hyvärinen O.** &Hämäläinen M. (2005).HydroCopper™ - a new technology producing copper directly from concentrate. Hydrometallurgy, 77, 61-65.
- Liang, C. L.**et al. (2010). Effect of activated carbon on chalcopyrite bioleaching with extreme thermophile Acidianusmanzaensis. Hydrometallurgy, 105(1-2): 179-185.
- Lundström, M.,** Aromaa, J., Forsén, O., Hyvärinen, O., & Barker, M. H. (2005).Leaching of chalcopyrite in cupric chloride solution. Hydrometallurgy, 77(1), 89-95.
- Majima, H.,** Awakura, Y., Hirato, T., & Tanaka, T. (1985).The leaching of chalcopyrite in ferric chloride and ferric sulfate solutions. Canadian Metallurgical Quarterly, 24(4), 283-291.
- Marsden, J. O.,** & House, C. I. (2006).Chemistry of Gold Extraction (2nd Edition). Society for Mining, Metallurgy, and Exploration (SME)
- McDougall, G. J.,** & Hancock, R. D. (1981).Gold complexes and activated carbon - A literature review. Gold Bulletin, 14(4), 138–153
- Muir, D. M.** (2002).Basic principles of chloride hydrometallurgy. Chloride Metallurgy, 2, 759-791.
- Nakazawa, H.,** Fujisawa, H. and Sato, H.(1998). Effect of activated carbon on the bioleaching of chalcopyrite concentrate. Int. J. Miner. Process., 55(2): 87-94.
- O'Malley, M. L.,**& Liddell, K. C. (1987). Leaching of CuFeS₂ by aqueous FeCl₃, HCl, and NaCl: effects of solution composition and limited oxidant. Metallurgical Transactions B, 18(3), 505-510.
- Padilla R.,**Girón D., and Ruiz M.C. (2005).Leaching of enargite in H₂SO₄–NaCl–O₂ media Hydrometallurgy, vol. 80, pp. 272-279.

- Padilla R.**, Rivas C. A., and Ruiz M.C. (2008). Kinetics of Pressure dissolution of enargite in sulfate-oxygen media. *Metallurgical and Materials Transactions B*, vol. 39, pp. 399-407.
- Park, K.-H.**, Lee, C.-H., Ryu, S.-K., & Yang, X. (2007). Zeta-potentials of oxygen and nitrogen enriched activated carbons for removal of copper ion. *Carbon Letters*, 8(4), 321–325.
- Radzinski R.** & Ghahremaninezhad A. (2015). Activated carbon-assisted oxidation of arsenic species in process solutions and waste waters: the oxidation reaction mechanism. COM 2014 - Conference of Metallurgists.
- Radzinski R.** (2017). An investigation into the activated carbon-catalyzed arsenic oxidation process MSc thesis, Queen's University, Canada.
- Riveros, P. A.**, and Dutrizac, J. E. (2008). The leaching of tennantite, tetrahedrite and enargite in acidic sulphate and chloride media. *Canadian Metallurgical Quarterly*, vol. 47, pp. 235–244.
- Wang, S.** (2005). Copper leaching from chalcopyrite concentrates. *JOM*, 57(7), 48-51.
- Watling, H. R.** "Chalcopyrite hydrometallurgy at atmospheric pressure: 2. Review of acidic chloride process options." *Hydrometallurgy* 146 (2014): 96-110.
- Wilson, J. P.**, & Fisher, W.W. (1981). Cupric chloride leaching of chalcopyrite. *JOM* 33.2: 52-57.
- Zhang, W.** & Gu, S. (2007). Catalytic effect of activated carbon on bioleaching of low-grade primary copper sulfide ores. *Transactions of Nonferrous Metals Society of China*, 17(5): 1123-1127.

APPENDIX A

Determination of copper recovery in leaching tests

The copper recovery in percentage is defined by the following expressions:

$$\text{Copper recovery \%} = \frac{WCu_{\text{extracted}}(g)}{WCu_{\text{total}}(g)} \times 100 \quad (\text{A.1})$$

Where $WCu_{\text{extracted}}$ represents the copper in the solution at t time which was calculated as follow

$$WCu_{\text{extracted}}(g) = \text{Result chemical analysis} \left(\frac{mg}{L} \right) \times Vol.t (L) \times \frac{1}{1000} \left(\frac{g}{mg} \right) - Cu_{\text{inicial}}(g) \quad (\text{A.2})$$

Cu_{inicial} represents the initial copper concentration in solution considering 4 g/L of copper and a solution volume of 1L

Vol_t represents the solution volume when the sample was taken at time t . In this way, when the first sample was taken from the reactor, the volume was 1 L. Then when sample 2 was taken, the total volume was $1L - 5 \times 10^{-3} L$, where $5 \times 10^{-3} L$ corresponds to the volume of each sample. The process was repeated considering the following times: 0,1, 3,6,12,24,36,48,60,72,84 and 96 hours, thus in the last sample was considered a total volume of $1L - 11 \times 5 \times 10^{-3} L$.

WCu_{total} represents the amount of copper in 50 g of minerals (chalcopyrite or enargite concentrate).

In this way the copper contained in the minerals was calculated as follows:

Copper contained in chalcopyrite concentrate

$$WCu(CuFeS_2)_{\text{total}}(g) = \text{Mass mineral}(g) \times \text{wt\%} \times \frac{MWCu \left(\frac{g}{mol} \right)}{MWCuFeS_2 \left(\frac{g}{mol} \right)} \quad (\text{A.3})$$

Copper contained in enargite concentrate

$$WCu(Cu_3AsS_4)_{\text{total}}(g) = \text{Mass mineral}(g) \times \text{wt\%} \times \frac{3 \times MWCu \left(\frac{g}{mol} \right)}{MWCu_3AsS_4 \left(\frac{g}{mol} \right)} \quad (\text{A.4})$$

(*) Iron and arsenic recoveries in leaching test were calculated similarly to copper recoveries obtained in (A.1)

Determination of copper absorbed into activated carbon in contact tests

The copper absorbed was calculated in percentage by the following expressions:

$$Cu_{absorbed} \% = \frac{Cu_{inicial}(\frac{g}{L}) * Vol_t(L) * \frac{1000}{1}(\frac{mg}{g}) - Cu_t(\frac{mg}{L}) * Vol_s}{Cu_{inicial}(\frac{g}{L}) * Volumen_i(L) * \frac{1000}{1}(\frac{mg}{g})} \times 100 \quad (A.5)$$

Where $Cu_{inicial}$ represents the initial copper concentration in solution considering 5 g/L of copper and a solution volume of 0.1L.

Vol_t represents the solution volume when the sample was taken at time t considering a sample volume of 5 mL (Vol_s) and the following time: 0, 5, 20, 60, 200, 300 and 360 min. Vol_t was calculated as the above section.

Cu_t represents the amount of copper measured in the solution.

(**) Iron and arsenic absorption in Figure 20 and 22 in contact test were calculated similarly to copper absorption obtained in (A.1)

Determination As oxidation in Figure 29

The percentage of As oxidation ((As(III) to As(V))) was estimated by the following expressions:

$$As_{oxidation} \% = \frac{As_{inicial}(\frac{g}{L}) * Vol_t(L) * \frac{1000}{1}(\frac{mg}{g}) - As_t^{3+}(\frac{mg}{L}) * Vol_s}{As_{inicial}(\frac{g}{L}) * Vol_t(L) * \frac{1000}{1}(\frac{mg}{g})} \times 100 \quad (A.6)$$

Where $As_{inicial}$ represents the initial arsenic concentration in solution considering 2 g/L of copper and a solution volume of 0.1L.

Vol_t represents the solution volume when the sample was taken at time t considering a sample volume of 5 mL (Vol_s) and the following time: 0, 5, 20, 60, 200, 300 and 360 min. Vol_t was calculated as the above section.

As_t^{3+} represents the amount of arsenite measured in the solution by titration.

