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ESTUDIO MECANÍSTICO DE LA LIXIVIACIÓN SELECTIVA DE  
ARSÉNICO EN CONCENTRADOS DE COBRE ENARGÉTICOS

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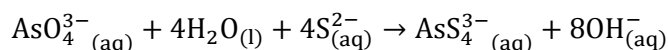
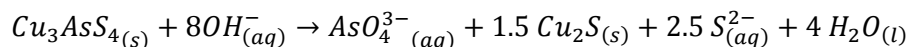
## ESTUDIO MECANÍSTICO DE LA LIXIVIACIÓN SELECTIVA DE ARSÉNICO EN CONCENTRADOS DE COBRE ENARGÉTICOS

La presencia de enargita en reservas de cobre asociadas a sistemas porfíricos es un problema conocido, el cual radica en la gran cantidad de cobre, sumado a la presencia de arsénico en su estructura. La presencia de arsénico dificulta el procesamiento de este mineral debido a su emisión al entorno durante el proceso. Entre muchas vías de procesamiento planteadas por diferentes autores, la lixiviación mediante sulfhidrato de sodio en medio alcalino se muestra prometedora, debido a que permite la separación selectiva del arsénico, dejando un residuo sólido con alto contenido de cobre y bajo en arsénico.

El propósito de este trabajo es dar a conocer detalles de la lixiviación de concentrados de cobre enargéticos. Para lo cual, el trabajo investigativo comprende una serie consecutiva de análisis teórico como experimental para seleccionar las mejores condiciones para el procesamiento del concentrado dispuesto y posteriormente para dilucidar un posible mecanismo de reacción, como es detallado a continuación.

i.- En primer lugar se realizó una revisión crítica del estado del arte respecto a los procesos de lixiviación de enargita, el cual se encuentra enfocado en sus fortalezas y debilidades con especial énfasis en los productos formados en la superficie del sólido. Es de esperar, hasta cierto punto, que las especies formadas en la superficie del mineral condicionen el desempeño del proceso y sean fundamentales si se quieren lograr conversiones cercanas al 100%. En el caso de la lixiviación en medio ácido, la estructura más reportada es azufre elemental, el cual dificulta en cierta medida el avance de la reacción. Por otro lado en medio alcalino se reportan resultados alentadores, razón por la cual se escogió para realizar los experimentos de laboratorio.

ii.- La lixiviación en medio alcalino se llevó a cabo utilizando una muestra de concentrado de cobre con calcosina, enargita y calcopirita como especies principales, proveniente de una mina en Chile. El desempeño del proceso fue evaluado mediante una cinética de reacción a 60°C y a 90°C. El proceso de lixiviación estudiado resultó ser altamente dependiente de la temperatura. A 60°C las extracciones de arsénico no superaron el 10%, mientras que para 90°C la recuperación se encuentra en torno al 80%. A su vez la energía de activación del proceso es 99.5 [kJ/mol] y el mejor ajuste cinético corresponde con un control mediante reacción química. A continuación se presenta el mecanismo de reacción propuesto para el sistema estudiado.



Tanto reacciones de oxidación de calcosina o calcopirita como de sulfidización de oxi-hidróxidos de cobre pueden ocurrir paralelamente. Adicionalmente, de manera inesperada, se midió la liberación de ácido sulfhídrico, alcanzando una concentración de 40 [ppm] en un recipiente de 55,7 [l] de volumen efectivo. Lo anterior puede deberse a la saturación de H<sub>2</sub>S en la solución, inhibiendo su redisolución. Teniendo en cuenta que esto reviste un problema para la implementación industrial del punto de vista de la seguridad operacional, se vislumbra como posible abatimiento de dichas emisiones, la implementación de un sistema mecánico que fuerce la redisolución del gas. Lo anterior surge de la disminución en 10 [ppm] (25%) de las emisiones de ácido sulfhídrico emitido mediante la implementación de un mecanismo de abrasión. Dicho sistema logra recuperaciones similares con respecto del tanque agitado pero la cinética de reacción es diferente.

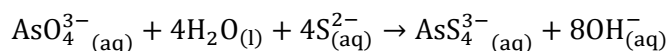
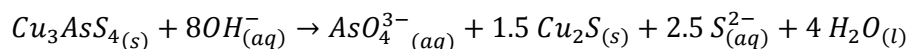
# Abstract

The occurrence of enargite ( $\text{Cu}_3\text{AsS}_4$ ) in porphyry copper ores is a well-known problem. The mineral contains in its structure a high amount of copper (economically valuable element), but also an important amount of arsenic. The latter makes the processing of ores bearing this mineral difficult as hazardous emissions of arsenic to the surroundings may be triggered during the implementation of the process. Among the many mineral processing paths proposed and tested by different authors, the use of alkaline sodium hydrosulphide solutions looks promising as it may separate selectively arsenic from the enargite structure leaving a solid with reduced quantities of the contaminant.

This research work aims at providing insights on the leaching of enargitic copper concentrate. The research consisted of a sequential series of theoretical and experimental steps primarily for selecting best conditions to treat this mineral and, subsequently, for obtaining insights on the reaction mechanisms embedded in the process, as follows:

i.- A critical review of the current knowledge about the leaching processes of enargite was performed. The critical analysis assessed the strengths and weaknesses of leaching processes of enargite with emphasis on the solid surface products built at the surface of the mineral during the leaching processes. It is expected, to some extent, that this surface structure and chemical composition may be relevant when pursuing a reaction conversion close to 100%. In acidic conditions, the surface structure reported by many authors was sulphur, which is difficult to overcome. The alkaline conditions show promising results and experiments using these conditions were carried out.

ii.- The leach reaction in alkaline conditions was studied experimentally at laboratory scale using an arsenic-bearing copper concentrate from a Chilean mine site. The reaction kinetics studies evaluated the performance of selective leaching process at 60 and 90°C. Main copper and arsenic bearing species in the ore were chalcocite, enargite and chalcopyrite. The process is highly dependent on temperature conditions. Arsenic extractions at 60°C were below 10% while near 80% recovery was achieved at 90°C. The overall reaction showed an activation energy of 99.5 [kJ/mol] and, then, chemical reaction kinetic control. The following mechanism was then proposed to explain the enargite alkaline sodium hydrosulphide leach:



Other parallel reactions such as chalcocite or chalcopyrite oxidation and copper or iron (hydr)oxides sulphidation might as well occur. Unexpectedly, the release of hydrogen sulphide was observed and measured, reaching a maximum concentration of 40 [ppm] within a 55,7 [l] effective atmosphere volume. Preliminary understanding indicates this may take place due to saturation of  $\text{H}_2\text{S}$  in the aqueous solution inhibiting the gas re-dissolution. Looking at the process implementation, this negative aspect from the safety point of view could be attenuated using some mechanical system forcing the gas to remain in the system. Then, a brand new abrasion rig was designed, implemented and tested. Using the abrasion rig the  $\text{H}_2\text{S}$  emission was 10 [ppm] (25%) lower than for the stirred tank. The final arsenic extraction in both cases was similar but exhibited different reaction kinetics.

Para quien esté dispuesto a escuchar y no tan solo oír

Para quien esté dispuesto a saborear y no solo comer

Para quien quiera rumear

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Dicen que para realizar obras de gran significancia es menester contar con una red de apoyo y sería una tarea titánica el siquiera aventurarse en solitario. Si bien no soy quien para dirimir el significado que estas hojas puedan tener para algún lector en tiempos venideros, para mí reviste, sin mayor vacilo, un momento culmine con la importancia que ello conlleva.

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# Chapter 1

## Introduction

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From a general perspective, whenever reaching deeper zones within a porphyry system, complex copper sulphides are more abundant. Moreover, copper grade diminishes and extraction of copper from said structures exhibit a challenge to mineral processing facilities.

One example of the latter within copper porphyry ores is the occurrence of enargite ( $\text{Cu}_3\text{AsS}_4$ ). The mineral contains a 48.4% of copper in its structure, which is even higher than the copper content in chalcopyrite ( $\text{CuFeS}_2$ ), the most common copper sulphide mineral in the world, making it highly attractive from a processing viewpoint. Nevertheless, the presence of arsenic in the mineral is 19% inducing inevitably a potential hazard for the environment.

Pyrometallurgical processing paths are nowadays the most widely used processing route for primary sulphides. Arsenic emissions in the form of gases or roasting powders are usual whenever processing enargite rich concentrates. Environmental regulations associated with industrial residues are turning increasingly strict; therefore, the presence of arsenic initially considered a potential source of contamination in the concentrate is now troublesome.

New and improved mineral processing operations for enargite bearing copper concentrates are required. Alternative processing paths have been suggested such as concentration via selective froth flotation or hydrometallurgical processes. The concentration of enargite via froth flotation is not a resolved issue and it is usually recovered collectively with other copper sulphides. Even in the case the selective flotation of enargite is achieved, this path does not resolve the problem of commercialising the copper contained in its structure. Hydrometallurgical paths have shown more potential towards solving the problem. The leach of enargite either natural or synthetic under several chemical environments has been a highly fruitful scientific topic.

Acidic and alkaline aqueous solutions with different leaching agents have been thoroughly studied in the past, however, strikingly the mining industry have not noticed all these progresses profusely reported in journals and technical conferences. The aim of this undergraduate thesis is to revisit this topic from two specific perspectives: (i) the study of the surface chemical composition and structure formed during the leaching processes and, (ii) the testing of a proof of concept experiment that may provide some light towards the process implementation. Both aspects are briefly explained in the next couple of paragraphs.

Tracing back in history the ore leaching occurs by definition at the solid-liquid interface where destabilised elements are spontaneously transferred to the solution. During the process, the reaction products may or may not dissolve. Solid product formation could result in particles that will remain suspended in the aqueous solution. Nevertheless, if the solids formed are stable in contact with the aqueous solution and adhere to the original particle, the solid structure could inhibit further reactions. That is the case when leaching reactions promotes the formation of sulphur in

acidic aqueous solutions. After revising the published literature on the surface reaction products identified when leaching enargite mineral or enargite-bearing ores, authors disagree in their observations. Then, the first stage of this research project revises all the arguments and results presented by authors so as to clarify this point.

Once identifying the most promising path to treat enargite bearing ores, the objective, at this point, is to take advantage from the knowledge associated to the reaction mechanisms, particularly the surface reaction products produced during the mineral leaching. Reasons for the non-implementation of the hydrometallurgical strategy will be pointed out and insights on the reaction mechanisms will be provided. It has been proved that many metal sulphides respond well to different mechanical activation and almost no information on the behaviour of enargite facing this treatment has been reported. Then, an experimental methodology will seek to improve the leaching kinetics via designing, implementing and testing a new rig focused on the application of abrasion mechanisms to enhance the process kinetics by mechanical activation.

## **1. General objective**

Analyse critically the scientific literature on enargite leaching to reach a consensus on what mediators are formed at the surface of the mineral so as to select the most promising conditions enabling to extract copper, arsenic or both and then, revisit the selected process to provide insights towards developing new and improve technologies to treat enargite bearing ores.

## **2. Specific objectives**

The specific objectives of this research study are:

2.1- Elaborate a critical review on the state of art of surface structures formed during the leaching of enargite (natural or synthetic) in order to reach a consensus on the published results.

2.2- Design and implement an experimental procedure (in this case, the selected process was alkaline sodium hydrosulphide based) for enargite leaching to study the associated reaction kinetics.

2.3- Develop an abrasion leaching proof of concept in order to find whether abrasion could enhance/inhibit the enargite leaching kinetics.

## **3. Scope**

The experimental part of this thesis only considers laboratory scale experiments on enargite-bearing concentrates submitted to alkaline sodium hydroxide leaching procedure. The research work did not take into account the treatment of the solutions containing dissolved copper and/or arsenic.

# Chapter 2

## Literature review

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### 1. Enargite occurrence

The presence of arsenic traces in the earth crust are not rare in nature; nevertheless, particularly high arsenic concentrations are often found associated with sulphide minerals [1]. The sulphide minerals, in many cases, consist of double salts, which are difficult to process when one of the elements is arsenic as it represent a potential risk of contamination during its processing. enargite mineral is one example of this situation.

Enargite ( $\text{Cu}_3\text{AsS}_4$ ) is a copper-arsenic sulfosalt and its occurrence is usually associated with gold and other copper sulphides prominently linked with high sulphidation epithermal systems [2]. In Chile, enargite is related to copper porphyry systems and therefore it may co-exist with chalcopyrite and other copper sulphides frequently observed in these mine sites. Examples of this situation are Chuquicamata, Escondida, among others [3].

The copper content in this ore, the co-existence with chalcopyrite and the simultaneous presence of arsenic in its structure raise a mayor problem to mineral processing specialists from an environmental standpoint. Moreover it complicates the mine planning because, at the present time, there is no knowledge available about a process enabling the processing of enargite enriched copper concentrates without exceeding environmental regulations or surpassing the maximum arsenic content in the cathodes.

Arsenic's environmental impact depends on the toxicity, aggregation state and stability of the compound or structure where the element is embedded [4].

### 2. Environmental legislation

Environmental legislation in Chile started with the foundation of an environmental management institution named "Comisión Nacional del Medioambiente" (CONAMA) and later, in 1994, the law of general environmental basis "Ley N°19.300" was officialised.

In 1995 the quality and emission rules regulation, which defines the meaning of pollutants and determines the concentration limits emission sources are subjected to, was approved.

The first arsenic emission rule was published in 1999 "Decreto 165" the limits published are indicated in the following table (Table 1) [5].

Table 1 Arsenic emission limits established in 1999

Location (Province/Region)	Production Capacity [ton/yr]	As [ton/yr]
El Loa/Antofagasta	$\geq 1.400.000$	1.100 (year 2000) 800 (since year 2001) 400 (since year 2003) <sup>1</sup>
Antofagasta/Antofagasta	$\geq 350.000$	126 (since 2000)
Copiapó/Atacama	$\geq 200.000$	42 (since 2000) 34 (since 2003)
Chañaral/Atacama	$\geq 500.000$	1.450 (year 2000) 800 (since 2001) 150 (since 2003) <sup>2</sup>
Elqui/Coquimbo	$\geq 80.000$	200 (since 2000)
San Felipe/Aconcagua	$\geq 350.000$	95 (since 2000)
Valparaíso/Valparaíso	$\geq 400.000$	120 (since 2000)
Cachapoal/Bernardo O'Higgins	$\geq 1.100.000$	1.880 (year 2000) 375 (since 2001)

As for any new facility installed the emission level should not exceed a 5% of total arsenic entering the premises and neither can be higher than 0.024% of total feed.

In addition, those new sources of arsenic installed in a zone influenced by an existing emission facility should control their emissions in order to assure the health protection levels in the surroundings.

As it was published in the “Diario Oficial”, in 2013, the new arsenic emission regulations provide a tougher scenario for enargite processing. This regulation indicates the following emission limits for existing refineries (Table 2) [6]. In this case, the criteria used to define the arsenic emission limits are based on a 95% capture and fixation due to cost-effectiveness considerations. In addition, arsenic emissions in furnace vent should not exceed 1 [mg/Nm<sup>3</sup>] for existing refineries and for new facilities they should incorporate the best technology available.

Eventually smelting facilities establish a critical arsenic content between 3.000 and 5.000 [ppm] when buying a concentrate. Higher arsenic concentrate are not saleable or penalties are applied [7].

<sup>1</sup> Applicable only if there are human settlements within an 8 km radius from the emission source.

<sup>2</sup> Applicable only if there are human settlements within a 2.5 km radius from the emission source.

Mechanistic study on the selective leaching of arsenic from enargite bearing copper concentrates

Table 2 Maximum limits of arsenic emission for existing sources

Emission Source	As [ton/yr]
Altonorte	126
Caletones	130
Chagres	35
Chuquicamata	476
Hernán Videla Lira	17
Potrerrillos	157
Ventanas	48

On the other hand, the maximum arsenic emission limit for new sources may not exceed the 2% wt. from total arsenic fed to the processing source for each calendar year.

### 3. Enargite processing in copper sulphide beneficiation plants

Enargite is processed as any other primary sulphide. After undertaking a comminution stage (crushing and grinding) the slurry is pumped to a froth flotation stage where copper enriched sulphides are selectively separated from the gangue and the final product is the copper concentrate, which is commonly commercialised to smelting companies.

In the mentioned process, the enargite is recovered in the concentrate together with primary copper sulphides minerals (chalcopyrite, bornite). At the present time, according to the scientific literature available, there are some reported results concerning the selective flotation of enargite, nevertheless, this study is still in its early stages. Consequently, the presence of enargite in copper concentrates will increase the arsenic grade in the concentrate, which is to be processed in the smelter facility.

In the field of pyrometallurgical processes, there are several technologies suitable for smelting copper concentrates. Particularly in Chile, batch reactors predominate (Teniente Converter, Peirce Smith Converter) over continuous processes (Mitsubishi, Flash) [8].

Batch smelter technologies allow fugitive emissions to the surroundings and considering the fact that an important fraction of the arsenic fed to the smelter volatilises, these emissions constitute a hazard to the surrounding biota [9].

Some companies have designed and implemented an intermediate roasting stage for copper concentrates, so as to reduce the arsenic content of the concentrate. But such designs were performed with some restrictions regarding the arsenic content and soon after the companies realised that the arsenic grade in concentrates fed to the process exceeded that threshold leaving the whole roasting operation unfunctional [10].

Another important aspect concerning the processing of arsenic bearing minerals is the safe disposal of materials containing the element [11]. As reviewed elsewhere arsenic disposal as calcium or ferric arsenate is unstable under atmospheric conditions or require high ferric or base metals addition. A safer disposal manner is precipitating arsenic as scorodite ( $FeAsO_4 \cdot 2H_2O$ ) but the further analysis of the arsenic disposal is out of the scope of this work.



## 4. Enargite chemistry

Enargite is a copper-arsenic sulphide with formula:  $\text{Cu}_3\text{AsS}_4$ . Its crystal arrangement consists in a wurtzite structure type where arsenic and copper replace one third and two thirds of zinc's atoms respectively. Some authors classify enargite as a sulfosalt and others differ from said denomination, as there are no  $\text{AsS}_3$  pyramids present in the structure [11].

Monovalent copper and pentavalent arsenic are the predominant oxidation states in this mineral [13, 14].

### 4.1. Enargite's reactivity in air

As any other sulphide minerals, enargite is unstable under aerated conditions and its reactivity is a key variable when analysing arsenic or copper extraction and defining a viable mineral processing route [12, 15, 16].

Considering enargite's reactivity when it is exposed to air at room temperature, arsenic atoms from the mineral surface tend to bond with oxygen alongside with copper partial oxidation. Bulk elemental oxidation is somehow slow. Higher temperatures would enhance the process development to some extent, especially across surface imperfections.

According to reported results, arsenic-oxygen bonding on the surface takes place rapidly forming a passivating layer with  $\text{As}_2\text{O}_3$  as the main arsenic specie [17-19].

### 4.2. Enargite's reactivity in solutions

Under acidic conditions, enargite is susceptible to oxidation [17, 20, 21]. This process can be rather slow at ambient temperature [13] but it is spontaneous. In this case, copper oxidises to  $\text{Cu}^{2+}$  and arsenic bonds with oxygen forming  $\text{AsO}_4^{3-}$ .

There are several studies involving enargite's dissolution and the best results are obtained at high temperatures and oxygen partial pressure or incorporating catalytic agents such as pyrite, activated carbon or silver [22-25].

On the other hand, when enargite mineral is immersed in alkaline aerated aqueous solutions, copper oxides and hydroxides are expected to form as well as arsenate ions [20, 26].

Moreover, in highly alkaline solutions mixed with sulphide or hypochlorite ions, arsenic selective leaching is achieved while a copper enriched sulphide is produced as a residue [27-34].

Since this undergraduate thesis is built in the form of a series of papers, more detailed information about the scientific literature available on the topic can be found in each one of the Chapters associated with the Results Section.

## 5. Mechanical fundamentals

This section is meant to provide a slight introduction towards mechanical processes in minerallurgy, as for the final part of this thesis incorporates results related to an abrasion proof of concept developed by the authors.

Mechanical processes play a key role on mineral processing as particle liberation results from crushing and grinding, nevertheless, they are not restricted to size reduction facilities [35-37].

Several efforts have addressed the use of mechanical process enhancement, thus sulphide activation being one practical example [38-40].

According to mineral comminution, there are different rock fracturing modes, some of which are: compression, impact, attrition, abrasion. These modes differ from each other mainly in energy applied, collision speed and inter particle interaction [35-37].

When designing size reduction equipment some of these fracturing modes is desired to predominate, nevertheless it is worth to keep in consideration that other fracturing modes would simultaneously occur as well [35-37].

Particularly in the sodium sulphide alkaline leaching process, attrition pre-treatment for 60 [min] in a planetary mill enhances reactivity of the sample, reaching full conversion well under 30 [min] leaching [30, 38, 41]<sup>3</sup>.

On the other hand, there are no published articles involving mechanical influences onto the particles, excluding mechanical stirring, during the leaching process.

Since this undergraduate thesis is built in the form of a series of papers, more detailed information about the scientific literature available on the topic can be found in each one of the Chapters associated with the Results Section.

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<sup>3</sup> The references of this chapter are listed in Chapter 9 General bibliography

Mechanistic study on the selective leaching of arsenic from enargite bearing copper concentrates

# Chapter 3

## General methodology

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The methodology followed in this thesis involves a thorough review of the state of the art of enargite leaching and data analysis of experimental results.

The critical review of the published scientific literature on leaching studies of enargite was carried out with emphasis in identifying the species formed on the outmost surface atomic layer of the enargite particles.

The alkaline sodium hydrosulphide leaching reaction for enargite was observed as one of the most promising processes and, therefore, experiments to assess its benefits were performed at laboratory scale. The solid phase used in this work consisted of an enargite bearing copper concentrate from a Chilean mine site. The concentrate consists mainly of chalcocite, enargite and chalcopyrite. The experiments were carried out at 60 and 90°C. Gaseous emissions, liquid samples, as well as, the residue were analysed.

A reaction mechanism is proposed resulting from the critical review and the experimental results obtained. Moreover, a thermodynamic analysis was undertaken to study its feasibility.

The details of the materials and methodology are specified on each Chapter according to the focus of each one of the scientific contributions presented in the manuscript.

# Chapter 4

## Leaching of enargite from the surface chemistry mediator perspective: a critical review

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### 1. Abstract

The sustainable processing of enargite ( $\text{Cu}_3\text{AsS}_4$ ) is a challenge the mining industry is dealing with nowadays. Several research efforts have been directed towards knowing the behaviour of this mineral under different chemical environments, so as to design improved mineral processing paths possible to implement at large scale and focused on both fixing arsenic avoiding environmental contamination and securing the commercialisation of copper, the valuable element present in its structure. This research study aims to review the surface reactions enargite mineral undergo when it is set in contact with different media with special emphasis on the reaction products formed at the mineral surface. The surface mediators.

In principle, according to the published literature, enargite is a double salt of Cu(I) and As(III). This has triggered efforts in hydrometallurgy towards implementing the extraction of one or both metals at different pH values via oxidation or reduction.

It was found that the most probable mediator under acidic conditions is elemental sulfur while under alkaline conditions are tenorite and arsenolite, as well as, copper and arsenic hydroxides. These mediator products are not in direct correlation with the thermodynamic diagrams presented in the literature. Further analysis towards taking advantage from this knowledge is presented.

### 2. Introduction

The simultaneous presence of arsenic and copper in enargite mineral structure is one of the most relevant challenges many copper concentrators are currently facing. To avoid penalties when commercialising copper concentrates, many companies have implemented blending strategies as no direct solution to this problem is available. As result of the latter, currently, enargite enriched copper minerals follow the same processing path as non-arsenic processing routes consisting in froth flotation, smelting, converting, refining and electro-refining. These processes still embed a number of difficulties to reduce the emissions of arsenic to the surroundings.

In addition, environmental regulations associated to the discarding of solids, liquid or gas streams containing arsenic are becoming stricter and the detrimental impact arsenic amounts have

in the quality of copper cathodes has forced the industry to seek alternative more sustainable processing routes. Several efforts have been directed towards roasting processes [1-4], nevertheless, hydrometallurgy has been suggested as a viable solution to this problem.

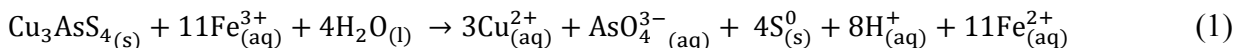
In order to design better processing routes, comprehensive knowledge on the reactions enargite undergo when facing different reagents in different media is required. Particularly, reactions occurring at the outmost surface layer of enargite are ill understood, not only due to the complexities present at an interface where non-stoichiometric structures may take place, but also due to the difficulties in identifying such structures with the present analytical techniques available. The aim of this study is to review the scientific information in the public domain on the matter and determine amongst all species reported by different authors, which ones are the most probable to occur, so to take advantage from it in designing new and improved processes. In the following, a review of different leach processes is provided with particular emphasis to the solid products composition and structure being formed at the enargite surface, which may promote or inhibit, or even stop, further extraction reactions.

### 3. Leach in acid aqueous solution media

Enargite leaching under acidic waters conditions has been extensively studied. Early studies reported slow recovery rates for copper and arsenic and classified enargite as a rather refractory mineral to leach processes; nevertheless, its reactivity in later research studies was shown to increase by increasing temperature, pressure or adding catalytic agents such as pyrite, silver and activated carbon [5-14].

#### 3.1. Case $Fe^{3+} + H_2SO_4$

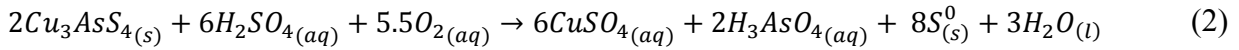
The leach of enargite using ferric sulphate in sulphuric acid medium at temperatures ranging 60 to 95°C was reported [6]. Arsenic extraction was not reported and copper extraction, although negligible, exhibited a linear behaviour with increasing time and a strong dependence on the temperature of the system. The activation energy of the reaction was 13.3 [kcal/mol], which is consistent with a chemical reaction control. The leaching residue was submitted to Soxhlet extraction, X-ray diffraction and optical microscopy. The residue consisted of elemental sulfur as the only solid product covering unreacted enargite particles. Then, acidic ferric sulphate leaching mechanism was represented as Equation (1).



Other tests of sulphate leaching of enargite adding sodium chloride in aerated media at temperatures ranging 80 to 100°C revealed similar results [7]. The influence of stirring speed, oxygen flow, acid concentration, chloride concentration, temperature and particle size on leaching kinetics was studied. Arsenic dissolution rate was slow and final extractions were as low as 6% and copper extraction was not reported.

The system exhibits a strong temperature dependence while the other reported variables had a minor influence on arsenic dissolution. Particularly stirring speed had no effect at 600 [rpm] or higher, likewise oxygen flow did not influence leaching kinetics over 0.15 [l/min]. Rising acid concentration in the interval (0.15 – 0.25 M) enhanced arsenic extraction. For higher acid concentrations the extraction drops. Chloride concentration increases the leaching rates in the whole interval studied (0 – 2 M), with decreasing influence for higher concentrations.

The mechanism was reported as Equation (2) and the solid residue was found to be unreacted enargite and elemental sulphur.

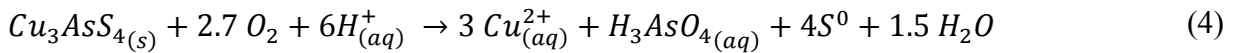
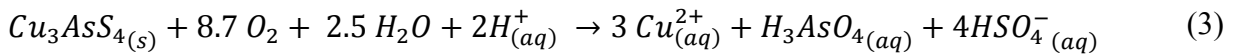


The activation energy of the system is 65 kJ/mol and the strong temperature dependence indicate chemical reaction as the kinetics controlling step [7].

### 3.2. Air pressure leach + $H_2SO_4$

Other study enquired about the acid sulphate pressure leaching of enargite at high temperatures. The process provided similar results to the experiments already detailed, but higher copper recoveries were obtained as the working temperature varied between 160 and 220 °C and simultaneously oxygen partial pressure ranged from 303 [kPa] to 1013 [kPa], Nevertheless, no arsenic extractions were reported.

The main reaction in this case is represented by Equation (3) and, also, Equation (4) occurs to some extent, especially at lower temperatures which explains the elemental sulphur formation [8].



The resulting activation energy is 69 [kJ/mol] and chemical reaction was concluded as the rate-determining step. A reaction kinetics model with a pseudo-order equals to 1/3 for oxygen partial pressure fitted well to the experimental data.

### 3.3. Sulphidation and subsequent air pressure + $H_2SO_4$

Another study involved the leaching of copper and arsenic from an enargite – chalcopyrite mixture by sulphidation and subsequent pressure acid sulfate leaching in aerated media. The sulphidation was undertaken at temperatures between 350 and 400°C resulting in chalcopyrite transformation into covellite and pyrite while enargite remains unaltered. The products of the sulphidation stage are later leached at temperatures ranging from 125 to 180°C and oxygen partial pressure varied between 507 and 1520 [kPa]. Copper and arsenic dissolution rates improved significantly, reaching full conversion at 180°C. The relevancy of oxygen partial pressure on the leaching kinetics is smaller under these conditions. Iron dissolution, in this case, was important. Other variables such as acid concentration and stirring speed had a negligible effect upon the extraction rate above 0.1 M  $H_2SO_4$  and 600 [rpm] [9].

In general terms, the leaching kinetics of pure enargite is less efficient than that of chalcopyrite-enargite mixture. This effect is explained in the paper by a catalytic effect between pyrite and enargite or by the generation of ferric ions acting then as an oxidant in the aqueous system. The activation energy resulting of the study is 71 [kJ/mol] and responds to a chemical reaction kinetic control [9].

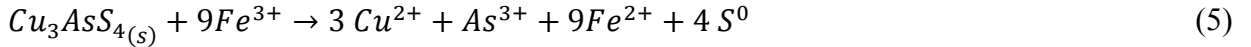
### 3.4. Sulphate Leach with catalysts

#### 3.4.1. Reducing agents such as activated carbon and pyrite

Ghanad (2011) studied the leaching of enargite in ferric sulfate solution at ambient pressure and 80°C catalysed by activated carbon [11]. Activated carbon was selected not only because of its large specific surface area, but also because it could create a galvanic couple with enargite enhancing the anodic reaction corresponding to enargite dissolution via oxidation [11]. The effects of solution redox potential, particle size, stirring speed and initial iron concentration were studied along with the influence of catalysts characteristics (type, amount, recycle) and the combined effect pyrite, silver and activated carbon were also addressed.

Both copper and arsenic reached nearly 100% extraction after 20 [h] leaching despite the formation of elemental sulphur promoted by activated carbon.

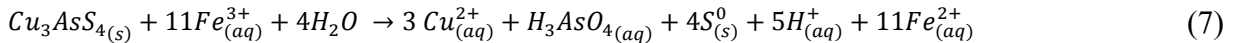
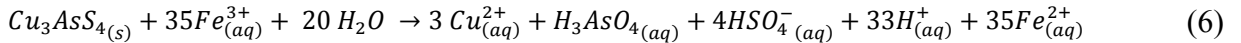
Equation (5) explains the leaching mechanism catalysed by activated carbon [11].



Ruiz (2011) studied enargite acid leaching catalysed by pyrite addition under pressure in the interval (345 – 1034 [kPa]) and temperature ranging from 160 to 200°C. At high temperature and oxygen pressure iron dissolves from pyrite and oxidises to ferric ions, which serves as an oxidising agent for enargite dissolution. This mechanism produces a sigmoidal extraction curve for copper and arsenic. The reaction rate is enhanced as iron concentration increases. Nonetheless, arsenic extraction is reduced at longer leaching times which may be associated to iron arsenate precipitation. No information was provided with respect to the reaction residues.

Temperature is a relevant variable followed by oxygen partial pressure. Other variables such as acid concentration and stirring speed have no influence above a threshold that avoids iron precipitation, particle settlement and oxygen availability in the solution.

Equations (6), (7) and (8) explain the experimental data. Equation (6) is the main reaction occurring at tested temperatures, Equation (7) takes place to some extent, particularly at lower temperatures, and Equation (8) defines ferrous ions oxidation.



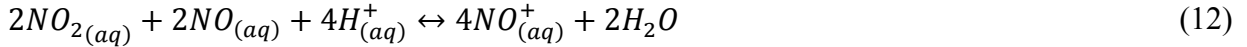
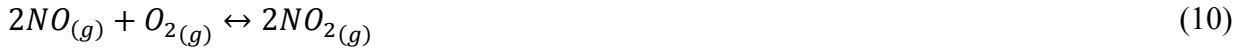
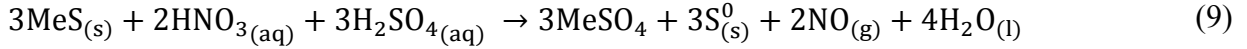
No activation energy was calculated for the exposed process, nevertheless chemical reaction kinetic control was fitted graphically.

Enargite dissolution under the same conditions without pyrite addition had a significant decrease on the leaching kinetics. The addition of ferrous ions enhances the leaching process but it exhibits a linear trend, as they were undertaken at a constant ferric concentration [10].

### 3.4.2. Oxidants such as nitric acid in autoclave

Nitrogen Species Catalysed (NSC) is an acidic catalysed leaching process. This process incorporates nitric acid or nitrous acid to form  $\text{NO}^+$  species to catalyse the dissolution. The process is undertaken in an autoclave type reactor and nitrogen species are regenerated. Equation (9) shows the mechanism of the process (Me refers to a metal) and Equations (10) to (12) explain the regeneration of  $\text{NO}^+$ .

NSC pressure leaching of enargite rich concentrates reports encouraging results and with proven industrial application in copper and silver ores [13, 15].

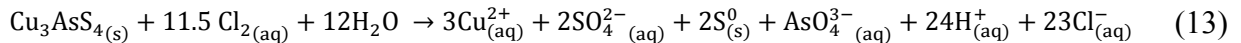


## 3.5. Other acid leaching procedures

### 3.5.1. $\text{Cl}_{2(g)}$ gas

The process is based on the reaction between chloride ( $\text{Cl}^-$ ) and hypochlorite ( $\text{ClO}^-$ ) to form chlorine ( $\text{Cl}_2$ ). The copper and arsenic extractions reached a maximum of 38% for fine enargite due to elemental sulphur coating. The temperature had a minor effect on leaching kinetics. Particle size, on the other hand, impacts significantly the leaching rate probably due to liberation.

The overall reaction of the in situ chlorine generation leaching is presented in Equation (13).



This reaction takes place in two steps, the first is a fast step (<30 [s]) controlled by mass transfer through liquid film with an activation energy of 15 [kJ/mol] followed by a slow step (>30 [s]) controlled by diffusion through a porous layer consisting of elemental sulphur and its activation energy is 21 [kJ/mol]. The first and the second steps' kinetics depend on chlorine concentration with pseudo-orders of 1 and 1.8, respectively.

The solid residue was analysed by SEM techniques and XRD concluding that elemental sulphur is formed as the only solid product. Half of the sulphide transforms into elemental sulphur and the other half is oxidised to sulphate [16].

### 3.5.2. Sulphatation and water leach

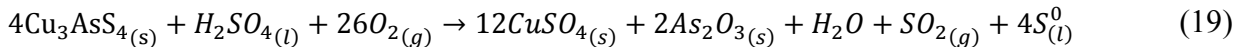
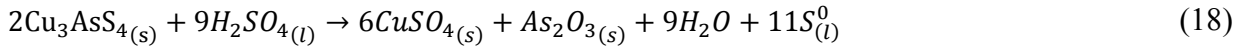
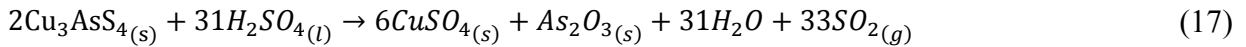
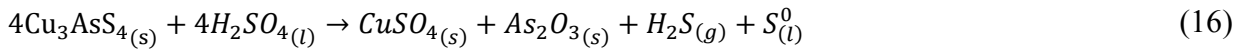
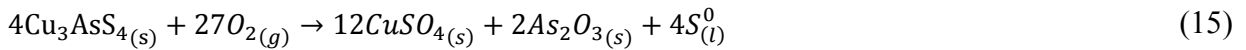
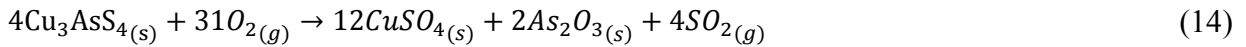
Acid sulphate bake and subsequent water leach process is postulated as a viable alternative to roasting, as it reduces arsenic emissions down to a minimum of 1%. The sample studied



incorporated enargite as the major phase (52.4%) as well as other species such as pyrite (10.3%), quartz (10.3%) and chalcopyrite (7.2%).

In the baking process, the sample is heated with concentrated sulphuric acid in a furnace at temperatures ranging from 100 to 200°C for 0.5 [h] to 7 [h]. Then, the product is immersed into deionised water for 45 [min]. When increasing the baking time from 0.5 [h] to 7 [h] at 200°C resulted in increasing copper, arsenic and iron extractions. Similar trend is observed when increasing temperature with constant baking time. Copper reached a 90% extraction while arsenic extraction was above 60% and iron extraction was close to 50%. Nevertheless, when increasing baking time up to 24 [h] at 170 °C reduces the extraction rate of the product in water and the arsenic volatilisation is favoured. SEM and EDAX analysis of the baking product resulted in copper sulphate formation on enargite particles surface. Also the leaching residue reported elemental sulphur formation and unreacted enargite particles.

It is probable that enargite transforms into copper sulphate and arsenic trioxide according to Equations (14 – 19) [12].



In summary, enargite leaching under acidic conditions is non-selective, highly dependent on the reaction temperature and the main residue formed is elemental sulphur.

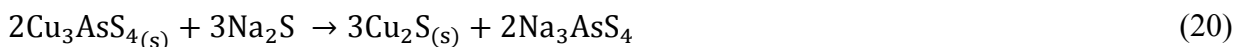
## 4. Alkaline solution leaching

Another enargite rich concentrate processing alternative consists in leaching within alkaline media. Two mechanisms with promising results are reviewed in detail: (i) sodium sulphide/sodium hydrosulphide and hydroxide leaching [13, 17-23] and (ii) hypochlorite and hydroxide leaching [24-26]

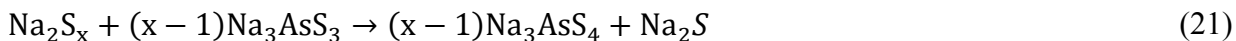
### 4.1. Alkaline sodium sulphide/sodium hydrosulphide leaching

Alkaline sodium sulphide leaching is a currently applied process in the antimony industry and emerges as a viable alternative to leach selectively arsenic from enargitic concentrates [17, 19, 20, 22, 23, 27-29]. Anderson and Twidwell published a kinetic study and a closed cycle optimisation in order to estimate associated costs of a hypothetical plant [13]. The study resulted in almost 100% arsenic dissolution after 4 [h] at 100°C, 300 [g/l] solids content in the slurry with 20 [g/l] sodium hydroxide and 40 [g/l] of sodium sulphide. Copper dissolution was negligible; antimony followed a similar trend to that of arsenic but to a lesser extent.

The reaction mechanism suggested was Equation (20).



The sulphide stable specie under these conditions is sulphide ( $\text{S}^{2-}$ ); nevertheless, other metastable species may coexist, such as polysulphides and thiosulphate. Hence, the stable arsenic specie proposed is thioarsenate according to Equation (21) [13, 20].



Further studies on the subject indicate a major influence of hydroxide concentration, temperature, sulphide concentration and particle specific surface on the leaching kinetics [17, 18, 21, 30].

Most of the published results justify hydroxide influence on leaching kinetics merely based on sulphide stabilisation [17, 18, 30]. A more relevant role of hydroxide ions on the leaching mechanism is suspected, though [23]. Curreli (2009) studied this system in an autoclave with oxygen partial pressure between 200 [kPa] and 250 [kPa], achieving complete arsenic removal after 2 [h] reaction.

The solid residue was later characterised through XRD and EPMA analysis, finding a non-stoichiometric copper rich sulphide ( $\text{Cu}_{1.5}\text{S}$ ) covering unreacted enargite particles [21].

Tongamp (2009) evaluated the kinetics of alkaline sodium hydrosulphide leaching in alkaline media. The sodium sulphide is replaced by sodium hydrosulphide to increase the sulphide content per mol of reagent. The experiments were undertaken at atmospheric pressure maintaining slurry pH and ORP at 12.5 and -500 [mV vs SHE]. Arsenic dissolution results were consistent with other published results, but As/S molar ratio exceeded 8 times the stoichiometry to reach a 0.5% or lower arsenic content in the concentrate.

XRD analysis of the leaching residue confirmed that enargite surface is transformed into  $\text{Cu}_2\text{S}$ , differing from  $\text{Cu}_{1.5}\text{S}$  previously proposed [17, 18]. Parada (2014) reported the formation of sodium copper sulphide ( $\text{NaCu}_5\text{S}_3$ ) as the main copper specie with tenorite ( $\text{CuO}$ ), bornite ( $\text{CuFeS}_4$ ) and Chalconatronite ( $\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3(\text{H}_2\text{O})$ ) [23].

A variation of this process involves mechanical activation through attrition prior leaching [19, 22, 30]. This pre-treatment allowed arsenic complete extraction at 90°C, 100 [g/l]  $\text{Na}_2\text{S}$  and 50 [g/l]  $\text{NaOH}$  after 10 [min]. The resulting activation energy of the process yielded 62 [kJ/mol]. For a process with 20 [g/l]  $\text{NaOH}$  the activation energy would increase to 182 [kJ/mol] [19, 22].

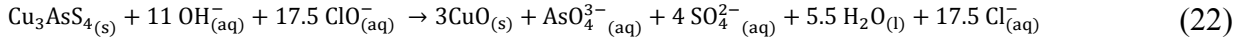
The remaining residues of activated samples leaching were submitted to XRD and XPS finding  $\text{CuS}$  (covellite), copper sulphide ( $\text{Cu}_{3.9}\text{S}_{2.8}$ ), jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) and chalcocite ( $\text{Cu}_2\text{S}$ ) [22, 27, 30].

The kinetic control has been reported to be diffusive due to a slight influence of the stirring speed on the leaching rate, but from the activation energy standpoint the reaction should be governed by chemical reaction [18].

## 4.2. Hypochlorite and hydroxide leaching

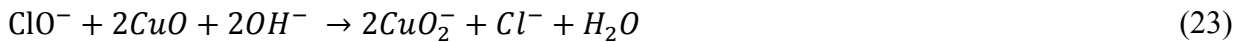
Hypochlorite alkaline enargite leaching involves a topo-chemical transformation of enargite into tenorite, while sulphur, arsenic and antimony are dissolved. Complete arsenic extraction is achieved after 40 [min] leaching time at 0.13 [M]  $\text{ClO}^-$ , 0.03 [M]  $\text{OH}^-$ , 1.13 [M]  $\text{Cl}^-$  and 60°C.

Viñals suggested the Equation (22) to explain the reaction stoichiometry.



In this case, enargite leaching kinetics is strongly influenced by temperature and particle size reduction with activation energy equal to 58 [kJ/mol]. The pseudo-order kinetics of hypochlorite concentration is 0.5, similarly to hydroxide concentration between 0.03 [M] and 0.003 [M]. For higher concentrations of hydroxyl ions, the hypochlorite decomposition is produced. Chlorine concentration and stirring speed had negligible effect on leaching.

Tenorite formed on enargite surface enhances hypochlorite decomposition at high pH values. This explains the decrease of extraction rate when hydroxide concentration exceeds 0.03 [M]. Equations (22) and (23) explain the mechanism.



The leaching residue analysis report copper oxide in the outmost surface layer followed by an arsenic deficient copper sulphide as an intermediate to unreacted enargite [24].

Curreli (2005) obtained nearly 92.5% arsenic extraction after 1 [h] using alkaline hypochlorite leaching of an Au-Cu concentrate. In summary, hypochlorite concentration, temperature, pH, particle size and solids concentration are the most influencing variables in this system [25]. Mihajlovic (2007) studied the hypochlorite leaching process in order to clean a high arsenic concentrate prior pyrometallurgical processing. High arsenic extractions were confirmed at 60°C after 2 [h] and a diffusion through a porous layer kinetics control is suggested with an activation energy of 30 [kJ/mol] [26].

## 5. Summary of leaching studies

Table 1 – 4 summarises the leaching parameters and characteristics of the reviewed studies.

Table 1 Summary of enargite leaching processes under acidic conditions reported in the literature; N: natural, S: synthetic, C: concentrate, M: mix

Leaching Media	Material	Reagents	Selective separation	Author
Ferric Sulfate	N/S	0.1 M H <sub>2</sub> SO <sub>4</sub> 0.1 M Fe <sup>3+</sup>	No	[6]
Hypochlorite + Hydrochloric acid	N	0.3 - 1.2 x 10 <sup>-2</sup> M Cl <sub>2</sub> 0.1 M HCl	No	[16]
Sodium Chloride + Sulfuric Acid	N	0.25 M H <sub>2</sub> SO <sub>4</sub> 1.5 M NaCl 0.3 l/min O <sub>2</sub>	No	[7]
Ferric Sulfate cathalised by Activated Carbon	N/C	53.3 g/l H <sub>2</sub> SO <sub>4</sub> 0 - 15.9 g Fe total 0 - 0.97 Fe <sup>3+</sup> /Fe <sup>2+</sup>	No	[11]
Sulfate Oxygen	N	0.1 - 0.5 M H <sub>2</sub> SO <sub>4</sub> 303 - 1013 kPa PO <sub>2</sub>	No	[8]
Nitrogen Species Catalyzed	C	2 - 3 g/l NO <sup>2-</sup> 25 g/l H <sub>2</sub> SO <sub>4</sub>	No	[13]
Sulphidation pre-treatment Sulfate Oxygen	N/M	0.1 - 0.3 M H <sub>2</sub> SO <sub>4</sub> 507 - 1520 kPa PO <sub>2</sub>	No	[9]
Sulfate Oxygen cathalised by pyrite	N	10 - 40 g/l H <sub>2</sub> SO <sub>4</sub> 345 - 1034 kPa PO <sub>2</sub> 40%w Pyrite	No	[10]
Sulfate Baking and water leaching	C	5 g/gCu H <sub>2</sub> SO <sub>4</sub>	No	[12]

Table 2 Summary of enargite leaching processes under alkaline conditions reported in the literature; N: natural, S: synthetic, C: concentrate, M: mix

Leaching Media	Material	Reagents	Selective separation	Author
Sodium Hypochlorite + Sodium Hydroxide	N	0.3 M NaClO 5 g/l NaOH	Until some extent	[26]
	N	0.07 - 0.47 M ClO <sup>-</sup> 0.003 - 0.03 M OH <sup>-</sup>	Until some extent	[24]
	N (C)	0.05 - 0.28 M ClO <sup>-</sup> 0.0003 - 0.03 M OH <sup>-</sup>	Until some extent	[25]
Mechanical pre-treatment Sodium Sulphide Sodium Hydroxide	C	100 g/l Na <sub>2</sub> S 50 g/l NaOH	Yes	[19, 22]
Sodium Sulphide Sodium Hydroxide	C	100 (40) g/l S <sup>2-</sup> 10 (20) g/l NaOH	Yes	[13, 20]
	N (C)	0.05 - 0.42 M Na <sub>2</sub> S 1.25 - 3.75 M NaOH	Yes	[21]
	N	0.5 - 1 M Na <sub>2</sub> S 1.5 - 3.5 M NaOH	Yes	[23]
Sodium Hydrosulphide Sodium Hydroxide	C (C/M/N)	0.68 - 1.35 (100 - 1000 g/l) M S <sup>2-</sup> 1.25 (100 - 1000 g/l) M NaOH	Yes	[17, 18]
Alkaline digestion and water leaching	N	2.66 - 5.31 M Na <sub>2</sub> S 2 - 4 M NaOH	Yes	[31]

Table 3 Summary of enargite leaching processes under acidic conditions reported in the literature continuation; AP: atmospheric pressure, NR: not reported, UD: unable to determine (Continuation)

<b>Kinetic Control</b>	<b>Temperature (°C)</b>	<b>Pressure (kPa)</b>	<b>Copper Recovery</b>	<b>Arsenic Recovery</b>	<b>Author</b>
Surface Chemical Reaction	60 - 90	AP	Low	Low	[6]
Mass transport /Difusion through porous layer	5 - 80	AP	Low	Low	[16]
Surface Chemical Reaction	80 - 100	AP	NR	Low	[7]
NR	80	AP	Reached full conversion	Reached full conversion	[11]
Chemical Reaction	160 - 220	303 - 1013	Reached full conversion	higher than 60%	[8]
NR	130	620	near 95%	near 95%	[13]
Chemical Reaction	Sulphidation 350 - 400 Leaching 125 - 180	507 - 1520	near 60% for enargite and near 90% for mixture	Reached full conversion for Mixture	[9]
Chemical Reaction	160 - 200	345 - 1034	Reached full conversion	near 95%	[10]
NR	100 - 200	AP	near 90%	near 60%	[12]

Table 4 Summary of enargite leaching processes under alkaline conditions reported in the literature continuation; AP: atmospheric pressure, NR: not reported, UD: unable to determine (Continuation)

<b>Kinetic Control</b>	<b>Temperature (°C)</b>	<b>Pressure (kPa)</b>	<b>Copper Recovery</b>	<b>Arsenic Recovery</b>	<b>Author</b>
NR	25 - 60	AP	NR	near 90%	[26]
Chemical Reaction	20 - 60	AP	NR	Reached full conversion	[24]
NR	20 - 45	AP	NR	near 90%	[25]
Chemical Reaction	60 / 80 / 90	AP	NR	near 90% with pre-treatment near 60% without pre-treatment	[19, 22]
NR	105 (100)	AP	NR	Reached full conversion	[13, 20]
NR	85 - 115	200 - 250	NR	Reached full conversion	[21]
Diffusion through product layer	25 - 90 (80)	AP	UD	Reached full conversion	[23]
Chemical Reaction	50 - 95	AP	NR	Reached full conversion	[17, 18]
Mass transport	60 - 90	AP	0%	near 97%	[31]

In summary acidic enargite leaching could reach desirable extraction values; nevertheless when selectivity is sought, alkaline leaching is the most viable route.

## 6. Enargite leaching from mediator perspective

Metal sulphide species are known to be unstable under atmospheric conditions [32-35]. Corrosion products are formed in the outmost surface layer. These surface species act as “mediators” and, depending on their stability, may or may not play a key role on the heterogeneous process enhancing or inhibiting it. Then, particularly in the case of enargite leaching the mediator analysis may be useful, not only to bring all studies published to one single framework, but also to seek consistency between thermodynamic data [36].

The studies comprised under the surface studies are mostly related to enargite’s flotation [37-45], therefore, oxidation products at different potentials and pH are thoroughly analysed. These results in conjunction with leaching reviewed data are indispensable for a better understanding of enargite behaviour in aqueous media.

## 6.1. Indirect or off-line surface species studies

This section comprises the studies involving indirect measuring techniques to determine the species formed at the mineral surface, therefore implying a higher level of data interpretation. ie, cyclic voltammetry, electrochemical impedance spectroscopy and zeta potential studies.

Under acidic pH conditions, enargite oxidation leads to copper dissolution in conjunction with a sulphur rich copper depleted layer formation at the particle surface. Elemental sulphur or polysulphide formation is inferred and sulphate formation at higher potential is expected. Copper at pH 4 and increasing potential could lead to CuO or Cu<sub>2</sub>S formation, as for arsenic species could be found as adsorbed H<sub>3</sub>AsO<sub>3</sub> or H<sub>2</sub>AsO<sub>4</sub> species [37, 44, 46].

In the pH range between 4.6 and 9.2 an arsenic sulphide layer and CuO precipitate in the particle surface. At pH 9.2 a copper arsenate (Cu<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>) passivating layer formation has been identified [37]. Moreover, the reduction of the oxidised layer formed at pH 9.2 could imply the formation of Cu<sub>2</sub>S and As<sub>2</sub>S<sub>2</sub> [37].

Under similar conditions at pH 9.2 CuO, As<sub>2</sub>O<sub>5</sub>, As<sub>2</sub>O<sub>3</sub> and CuSO<sub>4</sub> species are presumably formed and later confirmed by direct analysis. Sulphur binding energy changed, attributable to polysulphide formation [38].

Another published article at pH 10 indicates Cu<sup>2+</sup>, As<sub>2</sub>O<sub>3</sub>, CuSO<sub>4</sub> and CuS formation after submitting the sample to +869 [mV vs SHE] for 1800 seconds. Nevertheless, CuS formation is not definitive and might result from interferences in the spectra analysed [44].

## 6.2. Direct off-line surface species studies

As mentioned previously, surface species determined by XPS techniques or other outmost atomic layers chemical studies are considered a more direct analysis.

Under acidic conditions a copper depleted surface consensus is reached, nevertheless is arguable whether elemental sulphur or polysulphide is formed [44, 46-48]. Copper (II) and Arsenic (III) are the dominant metallic valences; nevertheless, As (V) was also found when Eh exceeds 0.6 [mV vs SHE] [46].

On the other hand, under alkaline conditions (pH > 10) surface studies report Cu(OH)<sub>2</sub>, CuO, As<sub>2</sub>O<sub>5</sub>, As<sub>2</sub>O<sub>3</sub>, CuSO<sub>4</sub> and Cu<sub>2</sub>S, thus the latter formed by electroreduction of the copper oxide surface layer [41, 44, 48]. Moreover, after alkaline sulphide leaching activated mechanically CuS was formed as solid residue [22].

## 7. Thermodynamic assessment

Pourbaix diagrams of sulphide species [20], copper-arsenic-sulphur-water system and copper-arsenic-water system [49] will be analysed in conjunction with Gibbs energy calculations to elucidate the feasibility of a certain reaction proposed in previous sections.

Figure 1 presents the stability diagram of sulphide species considering meta-stability and Figure 2 merges both Pourbaix diagrams of copper-arsenic-sulphur-water and copper-arsenic-water systems.



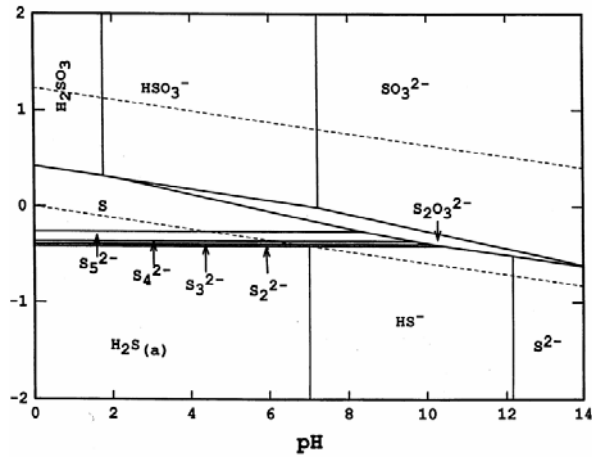


Figure 1 Meta-stable Eh-pH diagram for sulphur taken from [20]

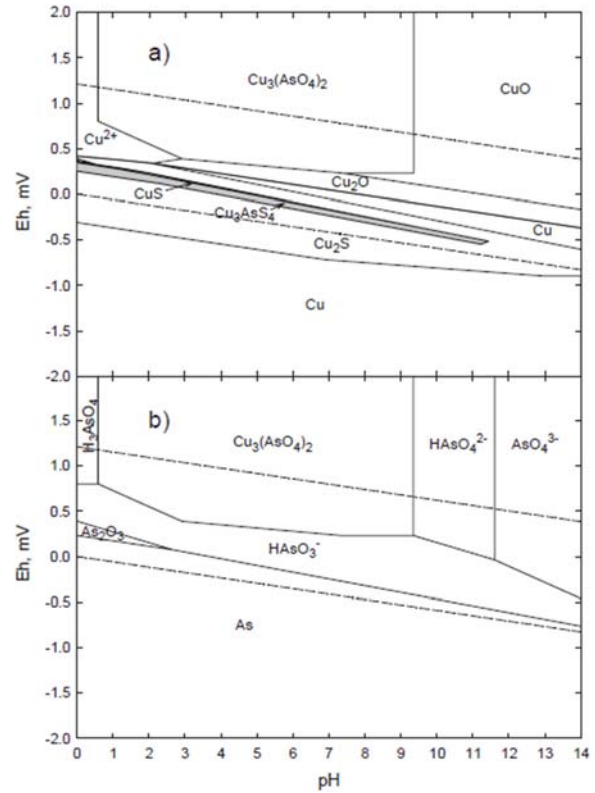


Figure 2 a) Pourbaix diagram for enargite in equilibrium with the Cu-As-S-H<sub>2</sub>O system at 25°C (1[M]) – b) Pourbaix diagram of the As-Cu-H<sub>2</sub>O system (1[M]) taken from [49]

According to the Pourbaix diagrams, arsenic soluble compounds prevail at pH values higher than 9. Nonetheless, copper and arsenic simultaneous extraction is possible under more acidic conditions.

## 8. Results and critical review

Table 5 summarise the mediators reported in several scientific publications under various conditions, in Annex A1 section are displayed the experimental details of the related publications.

Table 5 Summary of mediators reported in the literature; NA: Not Applicable, NR: Not Reported, RT: Room Temperature, CV: Cyclic Voltammetry, EIS: Electrochemical Impedance Spectroscopy

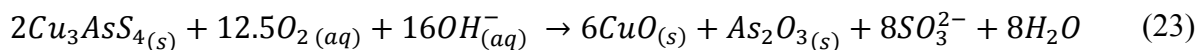
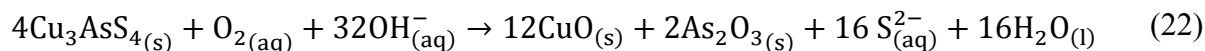
pH	Formulae (elem. Comp.)	Technique	Temperature	Author
9.2	As <sub>2</sub> O <sub>3</sub>	CV/EIS/XPS	25°C	[38, 39]
9.2	As <sub>2</sub> O <sub>5</sub>	CV/EIS/XPS	25°C	
9.2	CuO	CV/EIS/XPS	25°C	
9.2	Cu(OH) <sub>2</sub>	CV/EIS/XPS	25°C	
4.6 - 11	As <sub>2</sub> S <sub>2</sub>	CV/EIS	25°C	[37]
9.2	Cu <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	CV/EIS	25°C	
pH > 11	Cu <sub>2</sub> S	CV/EIS	25°C	
4.6 - 11	CuO	CV/EIS	25°C	
1	CuS	XRD	25°C/100°C	
NA	As <sub>2</sub> O <sub>3</sub>	XRD	25°C/100°C	[50]
NA	CuSO <sub>4</sub> ·5H <sub>2</sub> O	XRD	25°C/100°C	
13.7	Cu <sub>2</sub> S	XRD	25°C/80°C	[18]
13.7	CuS	XRD	60°C/80°C/90°C	[22]
1	S <sup>0</sup>	SEM	25°C	[16]
1	S <sup>0</sup>	Raman Spectroscopy	RT	[46]
2 - 8	S <sup>0</sup>	Soxhlet extraction	95°C	[6]
4	S <sup>0</sup>	XPS	25°C	
10	Cu(SO) <sub>4</sub>	XPS	25°C	[44, 45]
10	Cu(OH) <sub>2</sub>	XPS	25°C	
10	Cu <sub>2</sub> O	XPS	35°C	[45]
10	CuO	XPS	35°C	
11.5 - 12.5	CuO	XPS	25-60°C	
11.5 - 12.5	Cu(OH) <sub>2</sub>	XPS	25-60°C	[24]
11.5 - 12.5	As <sub>2</sub> O <sub>3</sub>	XPS	25-60°C	
NA	S <sup>0</sup>	XPS	25°C	[51]
11	As <sub>2</sub> O <sub>3</sub>	XPS	20-22°C	
11	As <sub>4</sub> S <sub>4</sub>	XPS	20-22°C	
11	As <sub>2</sub> S <sub>3</sub>	XPS	20-22°C	[41]
11	Cu(OH) <sub>2</sub>	XPS/ Electrophoresis	20-22°C	

The most observed mediators formed onto enargite outmost surface layer are:

- Alkaline media: CuO; As<sub>2</sub>O<sub>3</sub>; Cu(OH)<sub>2</sub>, AsO<sub>4</sub><sup>3-</sup>
- Acidic media: S<sup>0</sup>

According to the provided Pourbaix diagram (Figure 2) arsenic trioxide ( $\text{As}_2\text{O}_3$ ) is not stable at pH values higher than 3. Therefore, arsenic surface oxidation to arsenic trioxide would respond to a metastable phase, in contrast with the Pourbaix stable phase  $\text{AsO}_4^{3-}$  in the same region.

The following reactions (22 and 23) are proposed for arsenic trioxide ( $\text{As}_2\text{O}_3$ ) formation on enargite surface under alkaline conditions according to provided surface results.



The reaction Gibbs energy at 298 K is  $-2398$  [kcal/mol]<sup>4</sup> and  $-2560.8$  [kcal/mol] for reaction (22) and (23) respectively, implying its chemical feasibility and therefore, could be confirmed by a more thorough study of enargite solution chemistry.

## 9. Conclusions

The mediator formed in the outmost surface layer of enargite mineral depends on the pH of the aqueous solution the mineral is contacted with. Elemental sulphur is the most probable specie formed under acidic conditions associated with copper and arsenic content depletion during the process. Copper and arsenic oxide/hydroxide precipitates are most probable specie found when the leaching is conducted in alkaline solutions, moreover  $\text{AsO}_4^{3-}$  enables arsenic selective dissolution when leaching in alkaline sulphide solutions.

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<sup>4</sup> The reagents and products formation energies, enthalpies and entropies are indicated in the Annex A2 section.

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# Chapter 5

## Inadvertent release of hydrogen sulphide during alkaline leach of enargite-bearing copper concentrate

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### 1. Abstract

The presence of enargite ( $\text{Cu}_3\text{AsS}_4$ ) in copper sulphide ores is a well-known problem. The relatively significant content of copper in enargite mineral makes it economically attractive; however, the simultaneous content of arsenic in it is usually trouble for some mine sites, as it represents a potential source of contamination and it may lead to penalties during the commercialization of copper concentrates.

The use of alkaline sodium hydrosulphide solution, to selectively leach arsenic from enargitic copper concentrates has been suggested, by many authors, as a possible path to remove arsenic from the ore. Leaving a copper and sulphur enriched solid sulphide structure, therefore resolving this issue. This research work aims at studying at laboratory scale, the kinetics of arsenic extraction and simultaneous analysis of the gas atmosphere surrounding the aqueous solution, where the leaching reaction takes place. The latter was implemented as a precautionary measure due to safety considerations.

The experiments evaluated the leach of a Chilean copper concentrate with 3.8% As and a P80 of 29.98 [ $\mu\text{m}$ ] at 60°C and 90°C. The mineral analysis showed that the main species of copper are; chalcocite, enargite and chalcopyrite, and those of arsenic are; enargite and tennantite. It was found that arsenic extraction is highly dependent on temperature conditions. After 2[h] reaction, the arsenic extraction at 60°C was below 10% while at 90°C nearly 80% extraction was achieved. The activation energy of the process was 99.5 [kJ/mol] indicating chemical reaction kinetic control.

The most striking result observed during the experiments was the inadvertent formation and release of hydrogen sulphide gas. Stoichiometric analysis of sulphide concentration in the solution revealed, that hydrogen sulphide formation contribution to its consumption is worth noticing. A preliminar analysis of this situation indicates the gas release is related to; the local acidification at the solid-aqueous solution interface derived from the arsenic oxide formation summed with other reactions involving other sulphide minerals, along with the high concentration of sulphide ions, reducing the aqueous solution capabilities to re-dissolve the gas.



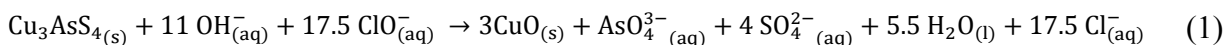
## 2. Introduction

Enargite ( $\text{Cu}_3\text{AsS}_4$ ) is a copper-arsenic sulphide found in porphyry ore systems. The relatively significant amount of copper in its structure makes possible its commercialization; nevertheless, its arsenic content turns this mineral into a potential source for contamination. Many solutions to this issue have been suggested such as; concentrate roasting, enargite selective flotation and design of new furnaces. In comparison with other techniques, the hydrometallurgy has exhibited promising results.

Early studies were focused on the leach of enargite, both synthetic and natural, using acidic ferric sulphate aqueous solutions [1]. Then, studies focused on determining the impact of different variables such as temperature, air/oxygen pressure, the presence of catalysts like nitrogen oxide ( $\text{NO}^+$ ) and other substrates (activated carbon, pyrite, etc) while using the same acid sulfate media have been published [1-5]. Moreover, acidic leaching has shown encouraging results in dissolving the metals from enargite under high pressure (303 – 1034 [kPa]) and high temperatures (160 – 220 °C) [2, 4] or at relatively low temperatures (80°C) and ambient pressure but incorporating activated carbon as a catalyst [5].

On the alkaline side, related to enargite's processing, two paths have been fruitfully published: (i) alkaline leach using hypochlorite as an oxidized agent [6-8] and (ii) alkaline leach assisted with sodium sulphide [9-16].

On one hand, the hypochlorite alkaline leach reaches high arsenic recoveries at ambient pressure and relatively low temperatures (below 100°C). The governing reaction is presented in Equation (1) [6].



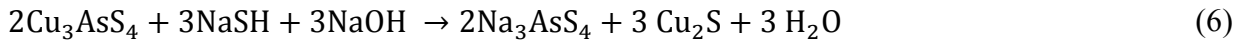
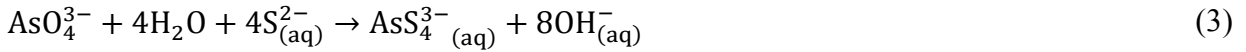
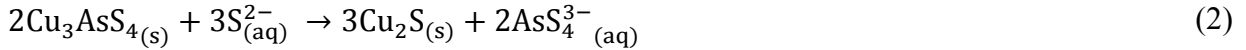
It has been found the temperature influences the reaction dynamics [7]; nevertheless, the reaction kinetics has been identified as slow and a diffusive mechanism governing the overall reaction has been proposed [8].

On the other hand, the sodium hydrosulphide alkaline leach exhibits promising arsenic extraction rates, reaching full conversion at temperatures below 110°C, as well as, at ambient pressure [9, 13, 16]. Another upside of this process is its selectivity: it dissolves preferably arsenic, antimony, gold and mercury but copper and silver [13].

Balaz (2000) studied the effect of attrition on arsenic extraction from enargitic concentrate samples using  $\text{Na}_2\text{S}$  alkaline aqueous solutions. The sample reached higher levels of arsenic solubilisation and the solid residue was found to be mainly covellite ( $\text{CuS}$ ). Moreover, the activation energy of the process was 62 [kJ/mol], which is consistent with chemical reaction kinetic control [15].

Curreli (2005) studied enargite sodium sulphide leaching mechanism applied to a gold bearing concentrate. Unlike Balaz (2000), Curreli (2005) reached to a copper/sulphur relation in the residue of 1.5 so the proposed residue by Curreli would be  $\text{Cu}_{1.5}\text{S}$ , stoichiometry between geerite and sponkiopite [14].

Equations (2-6) have been suggested in the literature to represent the alkaline leach of enargite assisted with sodium sulphide.



Relatively recent studies have highlighted the need for high alkalinity in the aqueous solution to reach significant arsenic extraction rates, avoiding the hydrolysis of  $\text{S}^{2-}$  ions [9, 10, 16]. However, no information has been published regarding probable changes in the gas phase composition due to the leach reaction conversion. This research work attempts to understand how the process may produce hydrogen sulphide and to which extent this can be related with the concentrate composition.

### 3. Materials and experimental methodology

A copper concentrate sample from a Chilean mine site was used to carry out hydrosulphide alkaline leach experiments. Silver, copper, arsenic, iron, antimony and bismuth elemental analysis were performed as well as automatic mineralogical analysis with QEMSCAN analyser Model Express®.

The ore leaching tests were conducted in a 750 [ml], 8 [cm] diameter mechanically stirred jacketed glass reactor, Remi Lab Stirrer|RQ-121/D (Figure 1). The heated water was pumped using a centrifugal pump, Iwaki Magnet Pump|MD-6-230GS01, through the jacketed compartment from a glass container equipped with a heater, Polyscience|7306A12E. The experimental system was placed into a glass box of known dimensions (66 [cm] x 40 [cm] x 31 [cm] and an effective volume of 55.7 [l]) where a hydrogen sulphide sensor ,MSA| Altair Pro 10074136, was placed to measure the gas concentration. The sensor detection range is 0 - 200 [ppm]. All the results reported were well above the detection limit.

During leaching experiments samples were extracted and filtered after 45, 60, 90 and 120 min. All the experiments were carried out in triplicate and average extraction results are reported. The samples were submitted to inductively coupled plasma – mass spectrometer (ICP-MS) analysis for trace elements and atomic absorption spectroscopy (AAS) for all other elements studied.

At the end of every leaching experiment, the pulp was filtered and washed with an alkaline solution similar to that used in the experiments. The solid was dried at 50°C under atmospheric conditions, pulverised and submitted to chemical analysis. The NaOH pellets used in the experiments were analytical grade and the NaSH solution was commercial grade with a 41.7% w. NaSH.

Both experiments, at 60°C and 90°C, were carried out in a solution containing; 87.4 NaSH [g/l], 50.4 NaOH [g/l] and 15% solids percent.

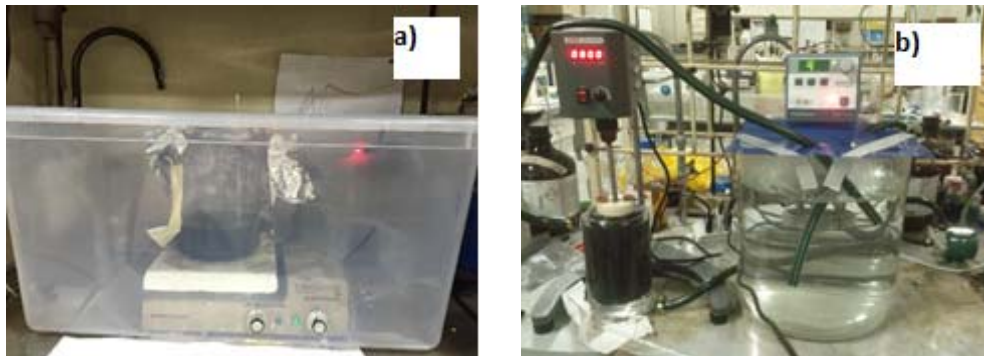


Figure 1 Pictures of the experimental setup a) glass-sealed stirred tank and b) Jacketed tank

## 4. Results and discussion

### 4.1. Ore sample characterisation

Table 1 presents the elemental analysis of the ore sample.

Table 1 Chemical analysis of the concentrate sample

Element [%]	Ore sample assay
Ag	0.06
As	3.8
Cu	32.5
Fe	11.5
Sb	0.3
Insoluble	21.2

Table 2 shows the mineralogical composition of the ore sample confirming the chemical analysis. The presence of copper is mainly due to presence of chalcocite (>50%) followed by chalcopyrite. The arsenic-bearing minerals are enargite (7.1%) and tennantite (below 1%).

Table 2 Concentrate sample mineralogical distribution, values in weight percentage

Minerals	Wt. %
Chalcocite	53.76
Chalcopyrite	5.79
Bornite	1.63
Covellite	0.59
Digenite	0.74
Molybdenite	0.05
Pyrite	16.80
Enargite	7.11
Other Sulphides	1.38
Tennantite	0.10
Quartz	1.95
Other Silicates	0.58
FeSulph	6.90
Others	2.63

Figure 2 presents the parity chart between the ore elemental assay and the elemental analysis estimated using automatic mineral analyser (QEMSCAN technique). The copper content is underestimated by QEMSCAN revealing some probable slight lack of liberation. Arsenic and iron departments exhibit good agreement between both techniques.

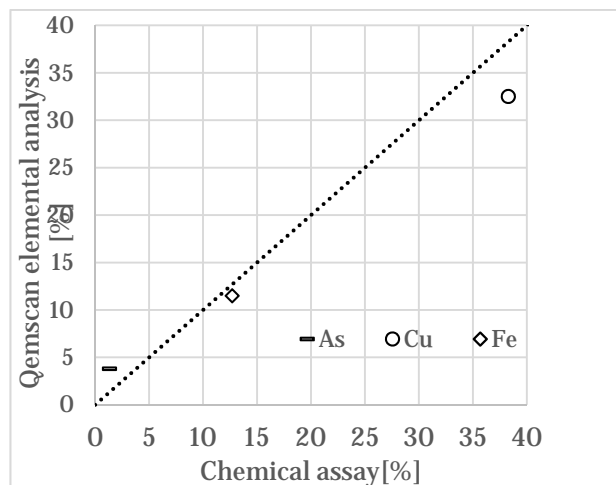


Figure 2 Elemental analysis comparison for copper, arsenic and iron content

Tables 3 and 4 present the distribution of copper and arsenic among the relevant minerals. Copper content is mainly procured by chalcocite and silicate minerals. A 95% of arsenic is present in the form of enargite and the remaining mass fraction is in the form of tennantite.

Table 3 Copper mineralogy distribution, values in copper wt. %

Minerals	Copper wt. %
Chalcocite	31.56
Chalcopyrite	1.99
Bornite	1.02
Covellite	0.39
Digenite	0.58
Enargite	3.44
Tennantite	0.05
Other Silicates	0.01
Others	0.01

Table 4 Arsenic mineralogy distribution, values in arsenic wt. %

Minerals	Arsenic wt. %
Enargite	1.35
Tennantite	0.02

The mineral association in the concentrate is presented in Figure 3. Enargite is mainly associated with chalcocite and covellite rather than with other sulphides.

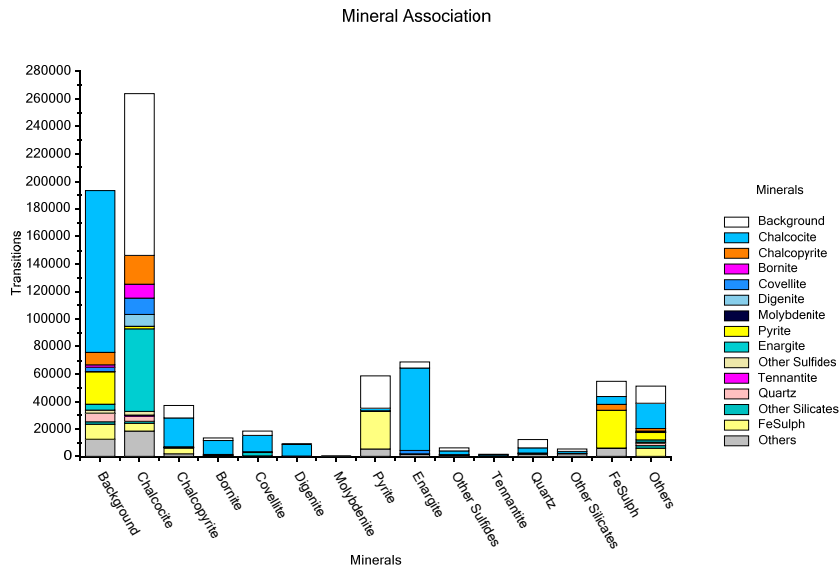


Figure 3 Minerals associations observed in the enargite-bearing copper concentrate

The liberation of arsenic bearing minerals are shown in Figure 4

Figure 4. The degree of liberation of arsenic species is as follows: 34% between 40 and 60% liberation, 50% between 20 and 40% liberation and the rest below 20% liberation. In the case

of copper bearing minerals, chalcocite exhibits a higher liberation compared to chalcopyrite (Annex A3).

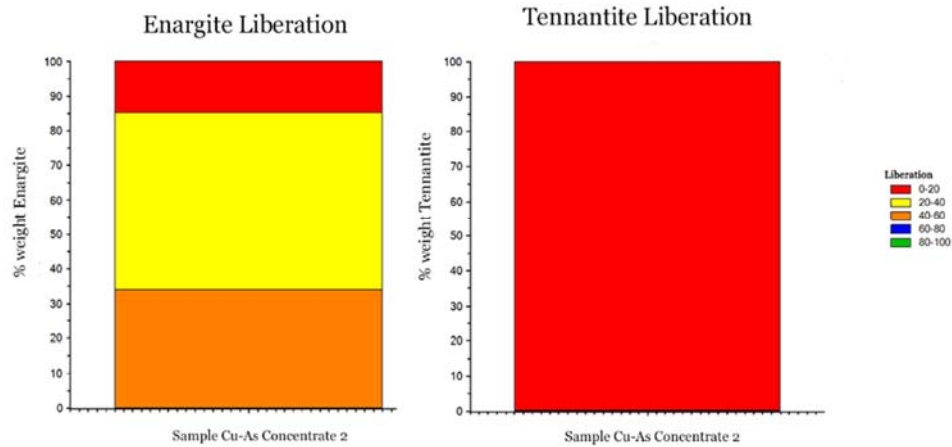


Figure 4 Degree of liberation for enargite and tennantite minerals in the copper concentrate

## 4.2. Ore leach results

### 4.2.1. Reaction kinetics and modelling

The following table (Table 5) displays arsenic as well as sulphur concentration during the kinetics study.

Table 5 Arsenic and sulphur concentrations in aqueous solution during leaching kinetics at 60°C and 90°C

Temperature	60°C		90°C	
	S [g/l]	As [g/l]	S [g/l]	As [g/l]
<b>0</b>	49.9	0.00	49.9	0.0
<b>45</b>	78.3	0.32	89.3	3.5
<b>60</b>	67.0	0.34	84.8	4.2
<b>90</b>	85.1	0.68	80.0	4.9
<b>120</b>	69.3	0.93	77.7	5.8

In all the tests, the concentration of arsenic in solution increases with time. The arsenic concentration after 120 min reaction, increased in more than 6 times when passing from 60 to 90°C. In the case of the leaching experiment performed at 60°C, the sulphur concentration is erratic while the results at 90°C can be analysed more clearly.

At 90°C sulphur concentration decreases with time after 45 [min] reaction. Figure 5 indicates the ratio between sulphide variation and arsenic extraction according to the reaction time intervals considered in the study.

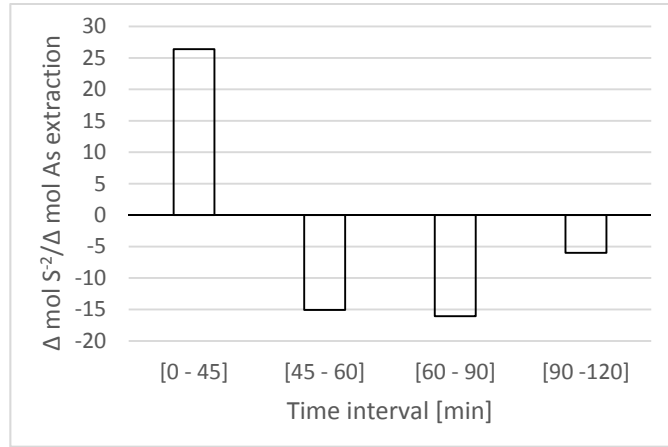


Figure 5 Experimental ratio between sulphide molar variation and arsenic molar extraction at 90°C; positive values indicate sulphide generation and negative values indicate sulphide consumption

According to the diagram, it is possible to distinguish 3 different reaction zones. The first zone associated to the first 45 [min] reaction is characterised by the generation of sulphide ions in solution and a  $\Delta S^{2-} \text{ variation} / \Delta \text{As extraction}$  molar ratio equal to 26. The second zone is related with sulphide consumption, which takes place between 45 and 90 [min] reaction. The absolute value of the molar ratio ranges between 15 and 16. Finally, the last reaction zone, from 90 until 120 [min] reaction, still exhibits sulphide consumption; nevertheless, the absolute value of the ratio decreases to around 6.

Table 6 shows the overall arsenic extractions as well as the copper, silver and arsenic concentrations remaining in the solid structure.

Table 6 Global extractions and tailings concentration of arsenic, copper and silver at 60°C and 90°C, values in percentage

	Leaching at 60°C	Leaching at 90°C
<b>As in tailings</b>	3.5 +/- 0.3	0.97 +/- 0.1
<b>Cu in tailings</b>	31.8 +/- 0.7	35.6 +/- 0.4
<b>Ag in tailings</b>	0.060 +/- 0.003	0.062 +/- 0.002
<b>As extraction</b>	11.99 +/- 3.4	77.3 +/- 3.02
<b>Cu extraction</b>	0.017 +/- 0.008	0.015 +/- 0.004
<b>Ag extraction</b>	6.7 +/- 0.1	12.3 +/- 0.08

The alkaline leaching kinetic results are presented in the Figures 6 – 9.

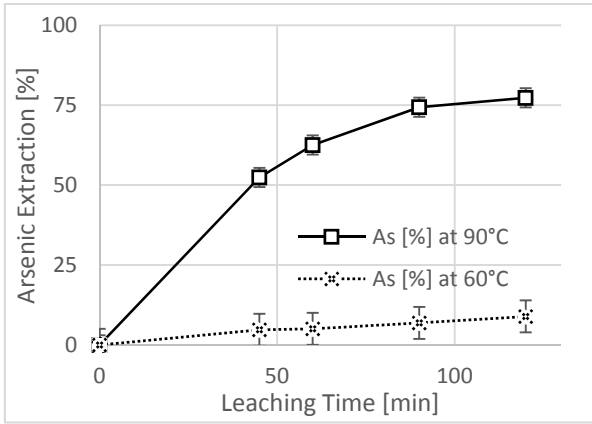


Figure 6 Arsenic extraction kinetics at 60°C and 90°C

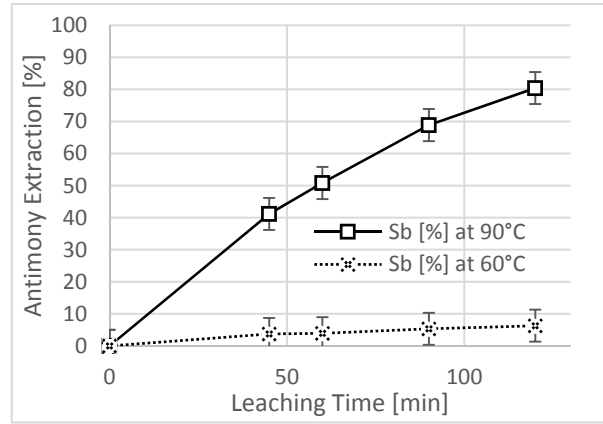


Figure 7 Antimony extraction kinetics at 60°C and 90°C

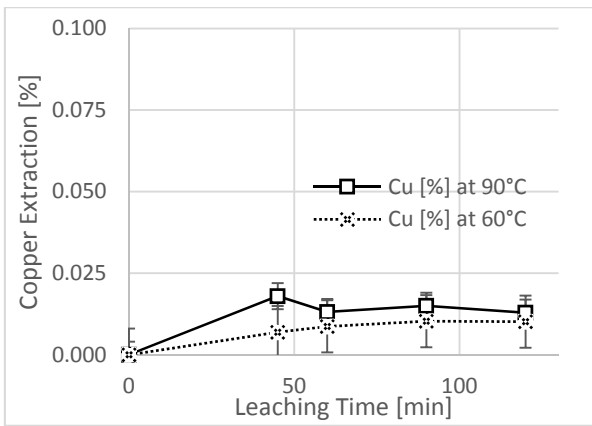


Figure 8 Copper extraction kinetics at 60°C and 90°C

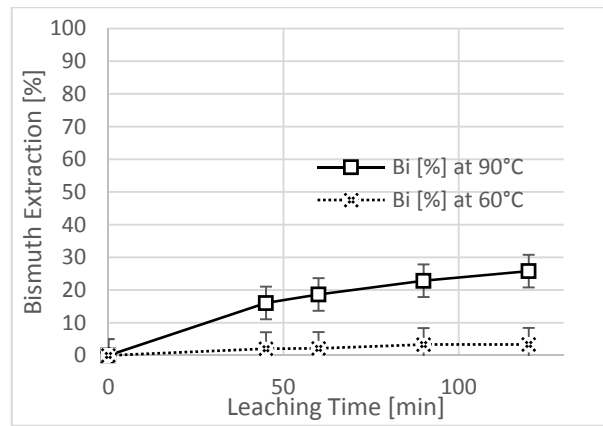


Figure 9 Bismuth extraction kinetics at 60°C and 90°C

The arsenic concentration increases with time. Its concentration does not reach a plateau after 120 [min] reaction, which may be an indication the extraction of the element could increase after the final reaction time considered in this research work (Figure 6). Tongamp et al, 2010 and Balaz et al, 2000 reported promising results for both leaching at 60°C and 90°C; nevertheless, they worked with natural enargite samples. It is expected that concentrate results will diminish. Still when leaching at 60°C the difference is abysmal.

On the other hand, Bujňáková et al, 2014 displays a better match with the reported kinetics and are more suitable as he worked with enargite concentrate.

Figures 10 and 11 present the fit of the shrinking core model to the experimental data.



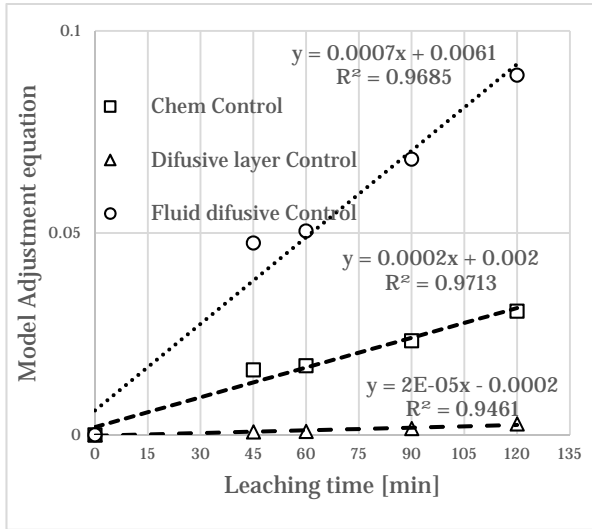


Figure 10 Rate controlling mechanism at 60°C

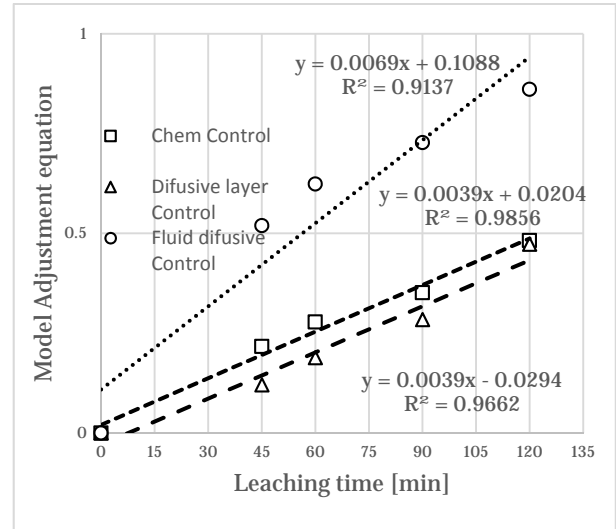


Figure 11 Rate controlling mechanism at 90°C

Despite all models provide an interesting fit, the closest adjustment applies to chemical reaction control at both temperatures. Summed to the previous results an Arrhenius plot was built to determine the activation energy of said process (see Annex A4), resulting in an activation energy of the system of  $E_a = 99.5$  [kJ/mol] consistent with chemical reaction kinetics control.

Antimony and bismuth concentrations in solution follow similar trends to that of arsenic. However, antimony reached extractions near 80% versus bismuth near 30% (Figures 7 and 9).

Copper extraction is almost negligible and its concentration with time is erratic, possibly due to very low copper concentrations or local acidity changes near the particle surroundings (Figure 8).

#### 4.2.2. Formation of H<sub>2</sub>S

During the leaching experiments, H<sub>2</sub>S emissions were detected, moreover at 90°C the concentration in the capsule was measured every 15 minutes. Figure 12 indicates H<sub>2</sub>S release kinetics.

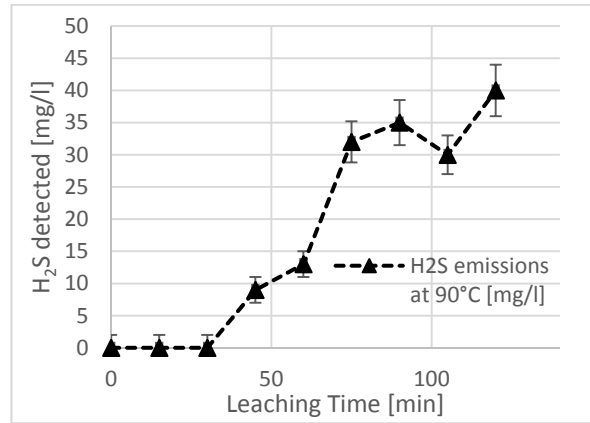
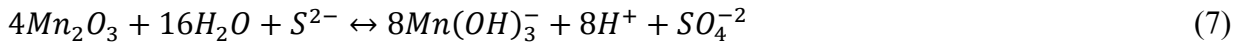


Figure 12 H<sub>2</sub>S release kinetics at 90°C

The chemistry of hydrogen sulphide in aqueous solution has been extensively reported. This can be explained by the Henry's law for H<sub>2</sub>S: the presence of a sulphide concentration close to that of saturation (or thermodynamic equilibrium) allows the formation of hydrogen sulphide without enabling its re-dissolution.

The local pH decrease could be associated with sulphate formation due to the reduction of polyvalent metallic ions forming anionic soluble species in alkaline conditions such as iron or manganese identified in the analysis of the aqueous solution. For example, from Pourbaix Diagrams, manganese may promote the acidification of the solution following the Equation 7.



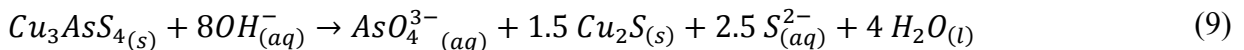
Certainly, reactions involving the neutralization reactions derived from the oxidation of surface sulphide minerals also can promote local acidic conditions. Furthermore, other alternative to produce local acidity may be related to the surface speciation of oxide species (Equation 8)

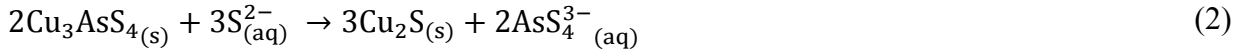
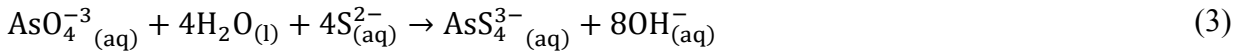


### 4.2.3. Effect of alkalinity on the leaching reaction

It is still an unknown, whether OH<sup>-</sup> influence on the leaching kinetics respond to adjusting pH avoiding sulphide hydrolysis or if it has a direct incidence on the leaching mechanism. Summed, the behaviour of enargite in a high ionic strength solution is rather unknown and complex. Therefore, a speciation analysis of the hydrosulphide ions under high ionic strength might provide valuable insight.

Integrating the surface mediators analysis detailed in the critical review with the observed leaching behaviour, result in the following proposed leaching mechanism for enargite leaching.





According to the suggested mechanism, the  $\text{OH}^-$  ions allow the formation of an arsenic oxide species at the mineral surface. The arsenic compound, is then, subsequently dissolved by sulphur ions.

The Gibbs energy of reaction (9) was calculated at 333 K and 363 K (60°C and 90°C) in order to determine its feasibility and influence in the leaching mechanism, resulting in  $\Delta G_{\text{rxn}}(363\text{K}) = -87.74$  [kcal/mol] and  $\Delta G_{\text{rxn}}(333\text{K}) = 7.94$  [kcal/mol].

Certainly, at 90°C the reaction Gibbs energy indicates it is probable to occur, however, at 60°C the resulting Gibbs energy is positive, indicating it does not occur; nevertheless its value is rather low.

The resulting pH from the system should be maintained; nevertheless, as reaction (9) implies acidification the particles surroundings could experience a local pH decrease and eventual  $\text{H}_2\text{S}$  formation.

According to the reactions (2, 3, 9-11); sulphide ions are formed according to reaction (9) and, then, they are consumed in reactions (3 and 10) while arsenic is transferred to the aqueous solution and hydrogen sulphide is released to the atmosphere. It is important to highlight that other reactions might occur simultaneously with other minerals present in the concentrate.

Therefore, these reactions proposed could explain, to some extent, the molar  $\Delta S^{-2} \text{ variation} / \Delta \text{As extraction}$  ratio observed in Figure 5. Moreover, the sulphide generation is attributed to reaction (9) and other oxidation reactions such as those proposed for chalcopyrite and chalcocite [17, 18]. The sulphide consumption involving sulphide to arsenic molar ratios near 15 is suitable via reactions 2 or 3 in conjunction with sulphidation reactions [19-23].

The final consumption stage of  $\text{S}^{2-}$ , exhibiting a sulphide to arsenic molar ratio of 6, indicates the predominance of reaction (2).

Equations 8 and 9 are side reactions occurring through the entire process, partially responsible for the overall  $\text{S}^{2-}$  consumption.

Figures 13, 14 and 15 present the governing reactions in each stage. Figures 13 and 14 consider the contribution of different reaction types to the variations in sulphide concentration; therefore, other unaccounted reactions are also taken into consideration. Moreover, these reactions, according to the concentrate composition, would possibly consist of chalcopyrite oxidation to ferric oxy-hydroxides, tenorite and its sulphidation [17-23].

Figure 15 indicates the contribution of the reactions 2, 3, 9-11 on the sulphide concentration changes along the considered reaction time.

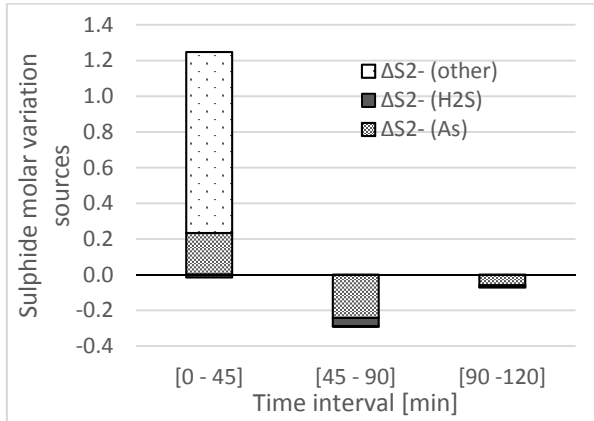


Figure 13  $S^{2-}$  variation sources chart;  $\Delta S^{2-}$ (As): Variation due to arsenic leaching mechanism reactions (7,2 or 3),  $\Delta S^{2-}$ (H<sub>2</sub>S): Consumption due to H<sub>2</sub>S formation (8 and 9),  $\Delta S^{2-}$ (other): Variation due to other parallel reactions; Negative variations indicate consumption and positive variation indicate generation

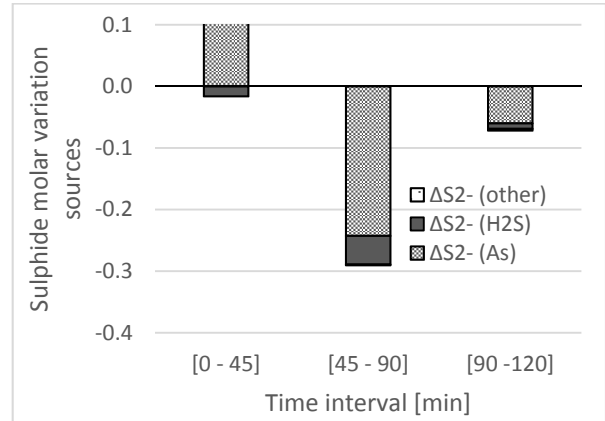


Figure 14 Zoom – in on Figure 13

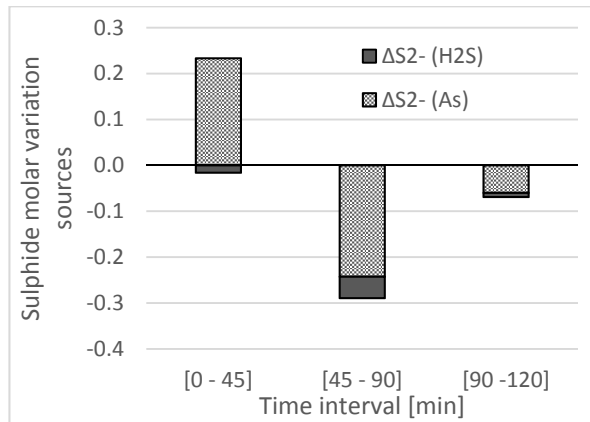


Figure 15  $S^{2-}$  variation sources chart;  $\Delta S^{2-}$ (As): Variation due to arsenic leaching mechanism reactions (7,2 or 3),  $\Delta S^{2-}$ (H<sub>2</sub>S): Consumption due to H<sub>2</sub>S formation (8 and 9); Negative variations indicate consumption and positive variation indicate generation

As it is indicated in the Figures 13-14, in the first zone (0-45 [min] reaction) the increase in sulphide concentration can be explained by oxidation reactions primary sulphides undergo similar to reaction (9).

In the second zone (45-90 [min] reaction) the change in sulphide concentration could be attributed to the thioarsenate formation (reaction 3), while sulphide consumption due to H<sub>2</sub>S formation increases significantly.

Later, in the final stage of the leaching process (90-120 [min] reaction), probably, the sulphide consumption is consistent with reaction (2) and other parallel reactions exerts almost no influence on the final concentration of the products in solution.

## 5. Conclusions

The selective leach of arsenic from arsenic-copper sulphide minerals was confirmed. The efficiency of arsenic extraction increased with the temperature in the temperature range between 60 and 90°C. The impact of temperature on the arsenic extraction, though, was in magnitude higher than several published results. Probably, this behaviour may be due to the concentrate mineral composition and associations within the ore used in the study which result in different reaction rates from what is observed for pure enargite mineral.

The hydroxyl ion concentration was observed as critical to achieve high arsenic extraction efficiencies.

Strikingly it was observed the formation and release of hydrogen sulphide in high alkaline conditions. This unexpected result can be explained by the local acidification of the solution at the mineral-solution interface promoting the nucleation and detachment of gas bubbles, which are not redissolved due to the saturating conditions of sulphide ions in solution. The latter, may be the main responsible for the release of the toxic gas.

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# Chapter 6

## Impact of abrasion mechanisms on the alkaline leach of enargitic concentrate

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### 1. Abstract

This research work aims at assessing the impact of abrasion mechanisms on the selective extraction of arsenic from enargitic copper concentrate via alkaline sulphide leach. Laboratory leach experiments were carried out in a jacketed stirred tank at 60 and 90°C and, at the same temperature conditions in a rig specially designed to apply abrasion over mineral particles. Hydrogen sulphide emissions were quantified using a gas detector. The results using both experimental setup were compared.

During the first minutes of reaction, the arsenic extraction kinetics was found to be notably slower than that observed in the stirred tank. The latter may be due to reactions occurring at the solution-stainless steel interface or other processes occurring on the surface mineral triggered by the energy input of abrasive mechanisms.

However, once reaching a reaction time threshold the rate increased significantly even reaching extractions similar to those observed in the stirred tank case, which might be an indication of mineral particle activation.

Perhaps, the most interesting finding is reduction in the emission of hydrogen sulphide in 25% when applying the abrasion on the particles.

### 2. Introduction

Enargite is a sulfosalt that commonly occurs in epithermal environments. In some cases the occurrence of this mineral is associated to major copper porphyry systems [1].

Whenever a copper beneficiation plant is implemented, the presence of this copper arsenic sulphide mineral represents a challenge not only from the point of view of the process but also environmentally as the mineral is a potential source for contamination. Particularly, the latter has forced the scientific community to search for alternatives to classic processes that allow meeting increasingly strict environmental regulations.

A hydrometallurgical path that utilises sulphide alkaline solutions to promote the selective extraction of arsenic from ores bearing enargite has been profusely reported [2-9]. Sulphide alkaline leach has been reported to extract nearly a 100% of arsenic from natural enargite samples at a temperature close to a 100°C and at ambient pressure. However, perhaps, the most significant



characteristic of this process is its selectivity making possible to extract arsenic, antimony, gold and mercury leaving other metals in the solid phase [6]. Although there are still unknowns related with the leaching mechanism all authors indicate the formation of a copper and sulphur enriched and arsenic deficient sulphide as a solid residue [2-9]. Recent studies have reported the inadvertent release of hydrogen sulphide gas to the air while carrying out alkaline sulphide leach of copper sulphide ore bearing enargite.

The release of a toxic gas while processing a copper ore demands robust safety standards during industrial implementation. It is well known that mechanical activation may produce changes in the reaction mechanisms when sulphide minerals are involved. Mechanical stress induces changes on the structure of the solid like increasing the density of defects on grain boundaries or changing the atomic arrangement, which are the principal responsible of higher reactivity of the solid rather than just the increase in solid specific area [10]. It has been previously stated that certain minerals activate under specific grinding conditions prior flotation as redox reactions take place in the mill [11, 12]. In hydrometallurgy, mechanical activation has also been studied as a sample clearly enhances its leaching rate after attrition for 60 min [4, 8, 13, 14]. All these results could be explained in terms of the mediators formed in the outmost surface layer of the particle which may determine the leaching performance; therefore, an abrading device would contribute to the particle surface mechanical clean up.

The aim of this research study is to assess the impact of abrasion mechanisms on the arsenic extraction kinetics and to test whether this mechanism will or will not reduce the hydrogen sulphide production.

### **3. Materials and experimental methods**

#### **3.1. Sample characterisation**

Alkaline leach tests were performed to an enargitic copper sulphide concentrate. The ore was submitted to chemical assay to measure the concentration of silver, copper, arsenic, iron, antimony and bismuth analysis. Automatic mineralogy, QEMSCAN model Express®, analysis was performed to another representative subsample.

#### **3.2. Experimental procedure**

Leaching experiments at laboratory scale were performed using a jacketed stirred tank and a rig specially designed to conduct tests applying abrasion to ore particles. The experiments were carried out at two temperature conditions: 60 and 90°C.

A 9 L abrasion mechanical device was designed and manufactured (Figure 1). The experimental conditions used in this study considered abrasion upon the mineral surface with a force of 20 N and a compression of 0.15 Pa. The temperature of the experiments was controlled using a heater and a thermometer with variations not higher than 5°C. Hydrogen sulphide emissions were measured using an off-gas exhaust with a H<sub>2</sub>S detector (MSA| Altair Pro 10074136).

Four samples of 10 mL were drawn from the leach solution with a sampling pipette and filtered at 45, 60, 90 and 120 min to study the reaction kinetics. The remaining pulp, then, was filtered and dried at 50°C and sent to chemical analysis to check the overall mass balance. The reaction kinetics results obtained with the jacketed stirred tank and the abrasion rig were compared.

All reagents used were high purity (>99%) but NaSH solution which was of commercial grade (41.7%w. NaSH).

The experiments undertaken at 60°C and 90°C, were carried out according to the following; 87.4 NaSH [g/l], 50.4 NaOH [g/l] and 15% Cp (solids percentage).



Figure 1 Pictures of the experimental layout

## 4. Results and discussion

### 4.1. Ore characterisation results

#### 4.1.1. Elemental analysis

Table 1 shows the results from chemical analysis for the concentrate samples are displayed. Bismuth values were not presented as its value was lower than the minimal detection limit (0.01 [%]).

Table 1 Chemical analysis of the concentrate sample

Chemical Analysis	
Element	Concentrate
Ag [ppm]	620
As [%]	3.8
Cu [%]	32.5
Fe [%]	11.5
Sb [%]	0.3
Insoluble [%]	21.2

#### 4.1.2. QEMSCAN analysis

QEMSCAN results indicate that the main mineralogical phases are chalcocite, pyrite and enargite. In addition, there is some evidence of chalcopyrite and tennantite (Figure 2). Figure 3 shows the parity chart between the elemental analysis provided by the QEMSCAN and the chemical assay techniques.

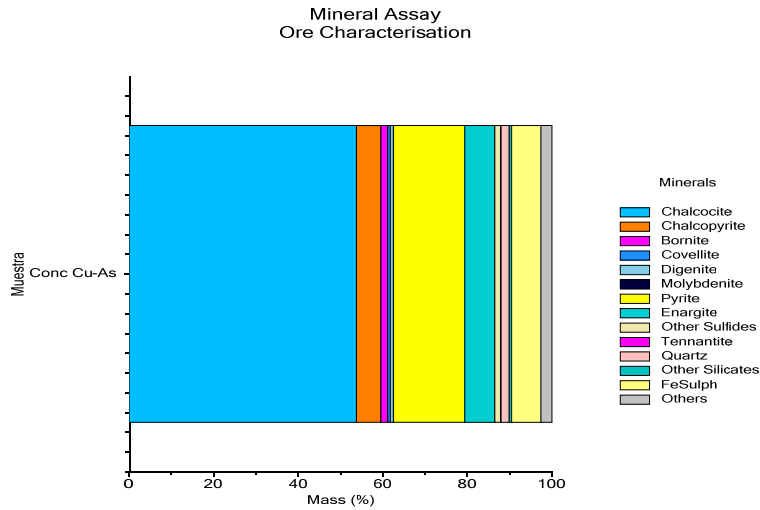


Figure 2 Distribution of minerals in ore sample

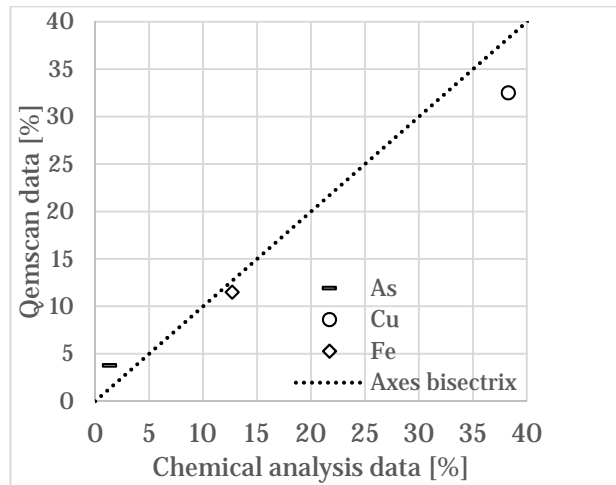


Figure 3 Elemental analysis comparison for copper, arsenic and iron content in ore sample

Qemscan analysis overestimated arsenic grade and underestimates copper and iron grades in the concentrate, but in general terms, both techniques provide consistent results

Figure 4 presents the modal mineralogy of the ore sample. On one hand, chalcocite and enargite are the predominating copper species followed by chalcopyrite and bornite. On the other hand, arsenic content in this concentrate can be attributed mainly to enargite.

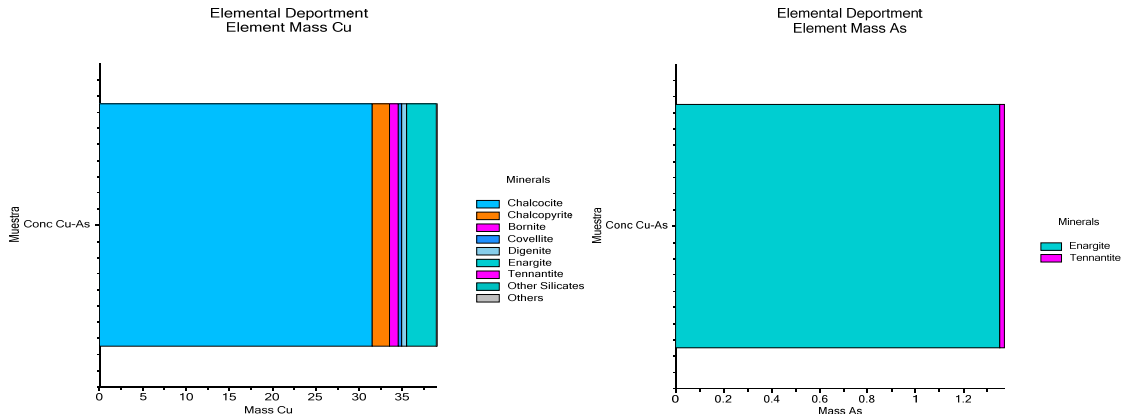


Figure 4 Copper and arsenic containing minerals in ore sample

The mineral associations are displayed in Figure 5. Enargite is mainly associated to chalcocite and covellite. Figures 6 and 7 indicate the liberation degree of arsenic associated minerals (enargite and tennantite) and non-arsenic copper main species (chalcopyrite and chalcocite). The average liberation of enargite ranges between 20 and 40% and its maximum liberation does not exceed a 60%, while tennantite liberation degree is lower than 20%. Moreover, copper bearing minerals exhibit higher liberation degrees reaching and average value between 80 and 100% for chalcocite.

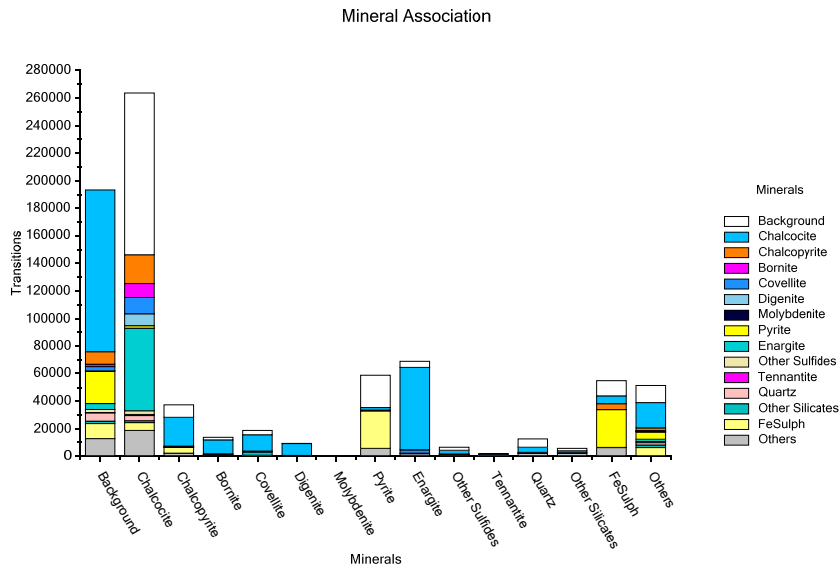


Figure 5 Mineral association in ore sample

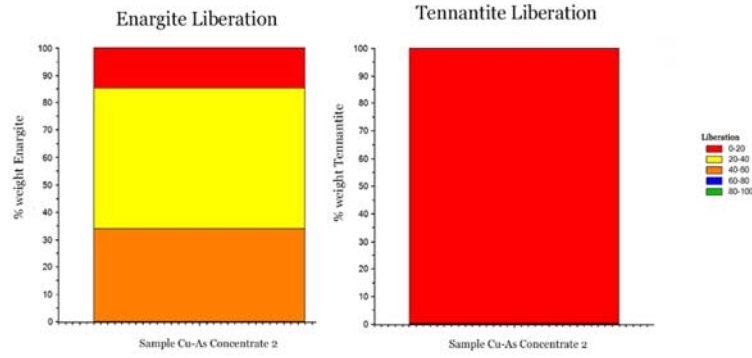


Figure 6 Enargite and tennantite liberation

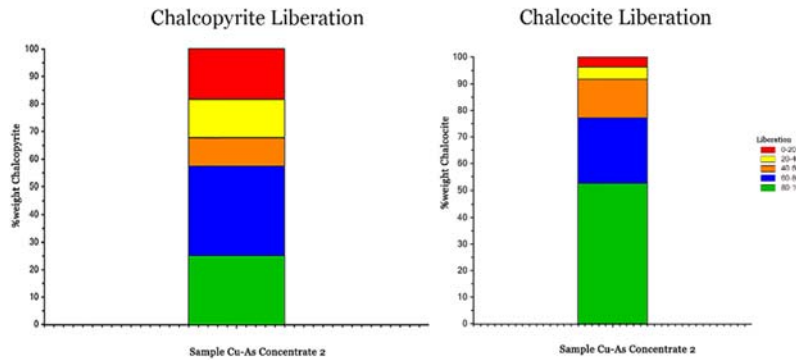


Figure 7 Chalcopyrite and chalcocite liberation

## 4.2. Enargite abrasion alkaline leaching

Figure 8 indicates the arsenic extraction curves at 60°C and 90°C for both, mechanically assisted and unassisted systems allowing the comparison between the arsenic extraction obtained using both rigs. Figure 9 provides a closer look into the systems behaviour.

At short leaching times (before 45 [min] reaction) the slope of the arsenic extraction curves at 60°C are similar, however, the efficiencies observed with the abrasion rig are lower compared to those obtained with the stirred tank. At 90°C the arsenic extraction with the abrasion rig is again below the stirred tank, but the extraction differences between the two experimental setup increases.

After 45 min reaction, the trends of arsenic extraction with the abrasion rig at both 60°C and 90°C, increases the slope. The slope of the extraction curves increase with the temperature where, for 90°C, the extractions reaches similar values to those exhibited with the stirred tank. The extraction value at 120 minutes reaction with the abrasion rig is rather associated to the experimental variability than to other factor.

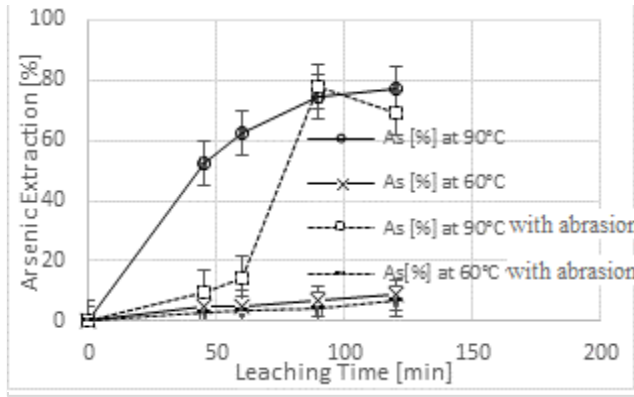


Figure 8 Alkaline leaching kinetics at 60°C and 90°C with and without abrasion (error bands were calculated for experiments without abrading mechanism and estimated for experiments with abrasion)

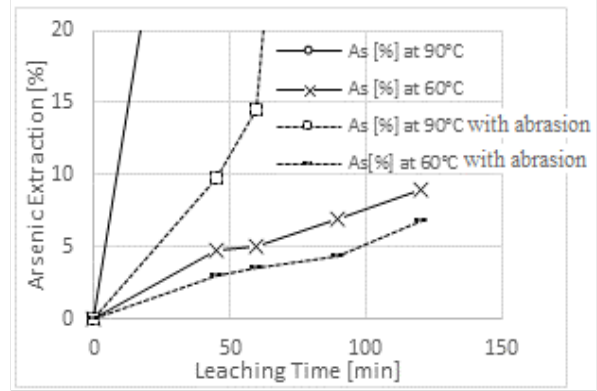


Figure 9 Zoom in to the leaching kinetics curve up to 20% arsenic extraction

The initial behaviour of the system could be influenced by stainless steel corrosion under caustic sulphide conditions, which is indeed enhanced with increasing temperature [15-17]. Moreover, the increasing extractions after 45 minutes in the mechanically assisted system, indicates the sample’s mechanical activation, as reported vastly. Abrasion coupled with other mechanical associated processes such as attrition or even compression would induce the activation of the sample studied.

### 4.3. Gaseous emissions

In the following figure (Figure 10) are indicated both H<sub>2</sub>S release curves of the 90°C experiments undertaken in the stirred reactor as well as in the abrasion rig.

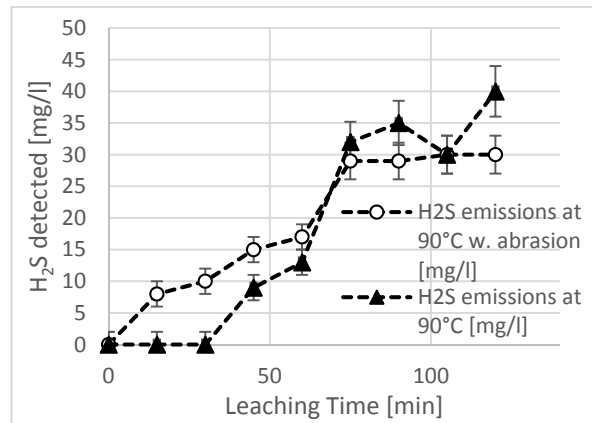


Figure 10 H<sub>2</sub>S emitted during the leaching experiments at 90°C

According to the data displayed in the Figure 10. Hydrogen sulphide (H<sub>2</sub>S) release behave differently under analysed circumstances. Moreover, the shape of the H<sub>2</sub>S release curve in the abrasion rig is similar to an exponential curve reaching a plateau, while the shape of the stirred reactor H<sub>2</sub>S release curve is similar to an “S” also reaching a plateau. It is noteworthy that, H<sub>2</sub>S final concentration was 10 ppm higher for the stirred reactor than for the abrasion rig, implying a decrease in 25% of the final gas concentration.

## 5. Conclusions

The selective arsenic leaching kinetic curves obtained in presence and in absence of abrasion mechanisms are different.

Before 45 [min] leaching time the arsenic leaching extractions in presence of abrasion were significantly lower than those obtained without the abrasion mechanism. This effect was found to enhance with increasing temperature. This is attributed to stainless steel passivation reactions running parallel to that of arsenic dissolution and probably other mechanical effects related to the compression of particles.

When reaching 45 [min] reaction, the slope of the arsenic extraction curve increases reaching similar extraction values of those observed in absence of abrasion.

A relevant aspect to take into consideration is that the hydrogen sulphide emission is considerably lower when applying the abrasion rig.

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# Chapter 7

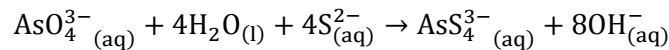
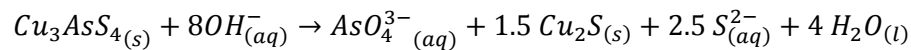
## Conclusions

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The following conclusion can be drawn from this study:

I.- The alkaline hydrogen sulphide leaching of enargitic copper concentrate selectively promotes the extraction of arsenic to the aqueous solution leaving a solid enriched in copper and sulphur.

II.- Based on the critical review and on the experimental results obtained at laboratory scale, the leaching reaction stoichiometry is in agreement with the following reaction mechanism:



III.- Despite reaching high recoveries at 90°C, those recovery values were below published results reported by other authors under similar laboratory experimental conditions. Probably this is because the relatively low enargite liberation degree, mineral associations and/or NaSH reagent grade.

IV.- The selective leaching of arsenic from enargitic copper concentrate is highly influenced by the temperature. The overall reaction activation energy of the process was found to be 99.5 [kJ/mol]

V.- The concentration of hydroxyl ions (OH<sup>-</sup>) on the leaching results was also essential to reach desired extractions. The proposed leaching mechanism indicates that OH<sup>-</sup> also assists the formation of AsO<sub>4</sub><sup>3-</sup> from enargite which is a precursor of thioarsenate (AsS<sub>4</sub><sup>3-</sup>).

VI.- The release of hydrogen sulphide during the leaching experiments was observed. The reason for this may be related to local acidification produced by the leaching reactions taking place at the surface of enargite mineral. In spite of the high concentration of sodium hydroxide, reagent commonly used in H<sub>2</sub>S scrubbers at industrial scale, the release of the toxic gas was identified and monitored. The latter may be related to the H<sub>2</sub>S saturation due to the high concentration of sulphide ions in the alkaline aqueous solution.

VII.- The release of H<sub>2</sub>S is somehow inhibited by the application of abrasion mechanisms to the particles during selective leaching of arsenic. The amount of released H<sub>2</sub>S is reduced in 25% compared to the leaching results obtained with the classic stirred tank setup.

# Chapter 8

## Recommendations for further work

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Related to enargite processing, particularly under alkaline sulphide media, there are unknown topics worth to study.

According to the influence of  $\text{OH}^-$  concentration on the leaching process, there is an abysmal difference when leaching at  $\text{OH}^-$  lower than 50.2 [g/l]. In order to define clearly the role of hydroxide ions within the system is recommended to analyse the variation of its concentration throughout the process. Liquid samples should be drawn and titrated in-situ.

Another recommended study is related to sulphide speciation within the system. It is expected that high sulphide concentrations would neglect hydrogen sulphide reabsorption, moreover, with increasing temperature the solubility of this gaseous product decreases. In order to find an optimum operational point between hydrogen sulphide formation and arsenic extraction is worth analysing a series of experiments varying sulphide initial concentration while monitoring the  $\text{H}_2\text{S}$  emissions within a closed atmosphere system at constant temperature.

Finally, the abrading system implemented on this publication exhibited a different behaviour than the unassisted system. Mechanical activation of enargite submitted to attrition has been reported previously, nevertheless the mechanical rig could exert, not only abrasion but also compression or other mechanical stress to the concentrate sample. Submitting the concentrate to compressive stress ranging 0.1 and 0.5 [Pa] while completely submerged to the leaching solution with similar  $\text{OH}^-$ ,  $\text{S}^{2-}$  and temperature as the abrading tests undertaken in this thesis.

# Chapter 9

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# Chapter 10

## Annexes

### 1. Annex A1: experimental conditions of reported mediators

Aqueous medium conditions	Observations/ Comments	Author
Agitated leach; solution [HCl]=0,5M	Ball milling and HCl leaching residue	[1]
NA	Ball milling in oxygen atmosphere/ High temperature (100°C) milling	
NA		
NaSH - NaOH enargite leaching	Sulfide concentration, hydroxide concentration, size effect, temperature and stirring rate were studied in order to provide a kinetics equation	[2]
400ml leaching solution 100g/l Na <sub>2</sub> S ; 50g/l NaOH; 4g Enargite	Alkaline leaching(stirring rate:500 min <sup>-1</sup> Leaching time:120 min) of a previously ball milled sample	[3]
Cl <sub>2</sub> /Cl <sup>-</sup> solution 1200 ml ; 0.3 · 10 <sup>-2</sup> M < [Cl <sub>2</sub> ] < 1.2 · 10 <sup>-2</sup> M; 2.1 g Enargite; ambient pressure	Sample was ground in porcelain mortar and hand classified/screened. 5 ml were withdrawn from the leaching process at certain times; Cu in solution analyzed by AAS	[4]
HCl solution	Cyclic voltammetry chronoamperometry	[5]
Sulfuric acid/ Ferric sulfate	Leaching	[6]
Sodium acetate and acetic acid glacial		
Disodium tetraborate decahydrate and sodium hydroxide	Surface species formation study at pH 4 and 10 in order to analyse particle hydrophobicity due to surface oxidation	[7, 8]
		[7]

Aqueous medium conditions	Observations/ Comments	Author
Hypochlorite solutions w. NaOH [OH] <sup>-</sup> =0,003 - 0,03 M; [OCl <sup>-</sup> ] = 0,07 - 0,47 M	Enargite leached in a ClO <sup>-</sup> /OH <sup>-</sup> media aiming for arsenic removal	[9]
NA		
NA	Oxidation in air	[10]
Conditioning at pH 11	Solution purged with N <sub>2</sub> for 20 min or with O <sub>2</sub> for 60 min	[11]
	Electrophoresis (pH 11 - 5 and backwards);	
0,05 M disodium tetraborate decahydrate; deoxygenated, deionized and decarbonated water	The sample was submitted to cyclic voltammetry	[12, 13]
HClO <sub>4</sub> /NaOH	Electrochemical oxidation 0,54 - 0,74 V vs SHE	[14]



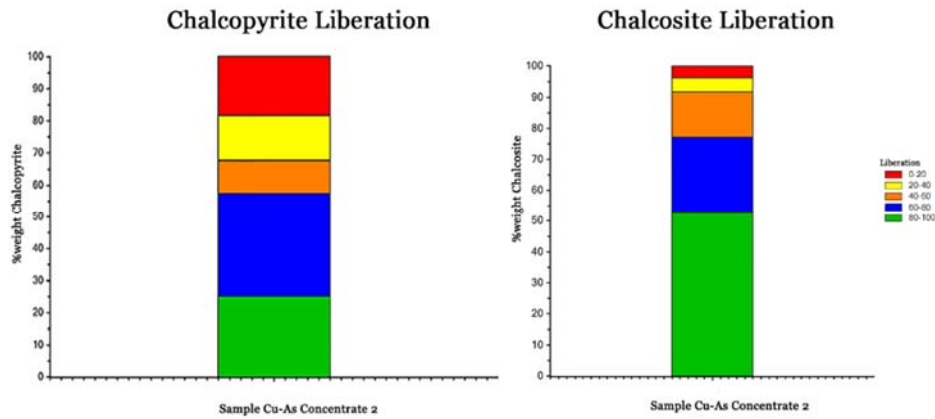
## 2. Annex A2: formation energies, enthalpies and entropies used for thermodynamic calculations

	$\Delta G^\circ_{298}$ [kcal/mol]	$\Delta G^\circ_{298}$ [J/mol]	$\Delta S^\circ_{298}$ [cal/mol K]	$\Delta S^\circ_{298}$ [J/mol K]	$\Delta H_{298}$ [kcal/mol]	$\Delta H_{298}$ [J/mol]
<b>AsO<sub>4</sub><sup>3-</sup></b>	-155.0	-648,954.0	-38.9	-162.9	-212.3	-88,873.2
<b>As<sub>2</sub>O<sub>3</sub></b>	-140.6	-588,664.1	27.9	116.8	-132.3	-55,386.7
<b>CuO</b>	-30.9	-129,455.9	10.2	42.7	-27.9	-11,674.2
<b>Cu<sub>2</sub>S</b>	-21.2	-88,760.2	28.9	121.0	-19.0	-7,954.9
<b>CuS</b>	-12.8	-53,591.0	15.9	66.6	-8.1	-3,375.3
<b>O<sub>2</sub></b>	0.0	0.0	49.0	205.2	14.6	6,114.2
<b>OH<sup>-</sup></b>	37.6	157,423.7	-2.6	-10.7	-55.0	-23,017.8
<b>H<sub>2</sub>O</b>	-56.7	-237,404.1	16.8	70.1	-68.3	-28,602.1
<b>S<sup>2-</sup></b>	20.4	85,452.6	-3.5	-14.5	7.9	3,311.8
<b>S</b>	0.1	376.8	7.8	32.6	2.4	1,008.4
<b>S</b>	0.0	0.0	7.6	31.9	2.3	952.0
<b>Cu(OH)<sub>2</sub></b>	-85.9	-359,604.3	20.0	83.7	-79.9	-33,465.1
<b>Covellite</b>	-11.7	-49,080.0	15.9	66.7	-7.0	-2,921.8
<b>Chalcosite</b>	-20.7	-86,868.0	28.8	120.8	-12.2	-5,088.5
<b>Enargite</b>	-9.52	-39,872.8	61.6	257.8	8.8	36,936.7
<b>SO<sub>3</sub><sup>2-</sup></b>	-149.81	-54,863.8	-7	-29.3	-151.9	-63,597.5
<b>AsS<sub>4</sub><sup>3-</sup></b>	-7.09	-29,665.07				

	$\Delta G^\circ_{363}$ [kcal/mol]	$\Delta G^\circ_{363}$ [J/mol]	$\Delta H_{363}$ [kcal/mol]	$\Delta H_{363}$ [J/mol]
<b>AsO<sub>4</sub><sup>3-</sup></b>	-259.4	-1,085,927.3	-273.5	-1,145,047.9
<b>Cu<sub>2</sub>S</b>	-10.0	-41,990.0	0.5	1,932.5
<b>OH<sup>-</sup></b>	-64.3	-269,098.3	-65.2	-272,989.0
<b>H<sub>2</sub>O</b>	-56.3	-235,646.9	-50.2	-210,190.1
<b>S<sup>2-</sup></b>	-46.3	-194,023.4	-47.6	-199,297.1
<b>Enargite</b>	-13.5	-56,426.3	8.87	37,136.9

	$\Delta G^\circ_{333}$ [kcal/mol]	$\Delta G^\circ_{333}$ [J/mol]	$\Delta H_{333}$ [kcal/mol]	$\Delta H_{333}$ [J/mol]
<b>AsO<sub>4</sub><sup>3-</sup></b>	-295.7	-1,085,927.3	-308.7	-1,292,451.1
<b>Cu<sub>2</sub>S</b>	-9.7	-41,990.0	-0.1	-430.9
<b>OH<sup>-</sup></b>	-78.5	-269,098.3	-79.4	-332,258.8
<b>H<sub>2</sub>O</b>	-55.9	-235,646.9	-50.3	-210,514.0
<b>S<sup>2-</sup></b>	-39.2	-194,023.4	-40.3	-168,912.3
<b>Enargite</b>	-11.6	-56,426.3	8.87	37,132.7

### 3. Annex A3: major copper species liberation



### 4. Annex A4: enargitic concentrate sodium hydrosulfide alkaline leaching

#### Arrhenius plot

