THE ALKALINE SODIUM SULPHIDE LEACHING OF ENARGITE

by

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Abstract

Leaching of enargite samples containing approximately 12 % As, 0.5 % Sb and 38 % Cu was studied in alkaline sodium sulphide solutions. Samples were leached in the presence of sodium hydroxide and sodium sulphide, which is expected to hydrolyse and form sodium hydrosulphide. Kinetic parameters studied included temperature, particle size, reagent concentration and stoichiometry in high pulp density tests. Leaching behaviour of arsenic and antimony was very similar; it was enhanced as temperature and reagent dosage was increased and/or particle size decreased. Copper, iron, zinc, and silver were not extracted during the leaching procedure. Through chemical analysis, X-Ray Diffraction and Scanning Electron Microscopy leach solutions and residues were characterised. Arsenic and antimony were efficiently removed, leaving copper-sulphur compounds such as digenite, bornite and sodium copper sulphide ($NaCu_5S_3$). Some of the leaching results differ from those found in the literature, especially in regards to the nature of the solid residue and the leaching reaction given.

Removal of arsenic from solution was analysed by acidification and crystallization. Acidification removed arsenic and antimony from solution to produce a mixture of oxides and sulphides; however, sulphide was removed from solution most likely as hydrogen sulphide, which would need to be scrubbed in a sodium hydroxide solution. Finally acid consumptions over arsenic plus antimony ratios were too large for a practical application. Crystallization on the other hand is a simpler alternative. The main requirement is to have high concentrations of arsenic and antimony in solution. In this case part of the arsenic and antimony would be recirculated to the leaching stage.

Other aspects included behaviour of chalcopyrite and pyrite in alkaline solutions and the possibility of producing sulphide ions in situ. Unfortunately no considerable amounts of aqueous sulphide were produced. Also, the behaviour of arsenic and antimony (III) in sodium sulphide alkaline solutions was analysed using arsenic and antimony trioxide. These results are in an early phase of study and could be a relevant

topic for further research. In both cases a black precipitate formed containing elemental antimony and oxides. However, no crystallization of thio-compounds seemed to have occurred.

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"...tú eres mi vida y mi felicidad..."

Chapter 1 Introduction

Copper is mainly extracted from sulphide minerals such as chalcopyrite ($CuFeS_2$), but it can often be associated with arsenic in sulphosalts. The most common of these sulphosalts is enargite (Cu_3AsS_4), and there are several copper deposits which have been or are being processed right now. El Indio in Chile, Lepanto in the Philippines, Chelopech in Bulgaria, etc. are examples of such deposits (Filippou 2007). Processing of copper ores (or any ores) that contain arsenic will face several issues; arsenic is considered a carcinogen with high mobility in aqueous streams, which in time may lead to arsenic in rivers (Oyarzun 2004-2006) and drinking water. In fact, there are several cases in which arsenic has been determined as the cause for massive poisoning and multiple cancer cases, like in Bangladesh, Thailand, Hungary, etc. (Jones 2008) and there are many studies that aim to remove arsenic from possible drinking water sources and contaminated soil (Hasegawa 1994, Chapell 1995).

Also, pyrometallurgical operations will penalize concentrates that contain arsenic over 0.5 % by weight, or even less depending on the operation. The presence of arsenic can also increase shipping costs of concentrates, which are commonly imported/exported overseas (Filippou 2007, Castro 2008).

Health and environmental concerns have produced a series of changes in regards to the control of arsenic exposure. In the United States, the EPA has lowered the maximum contaminant level (MCL) of arsenic in drinking water from 50 ppb to 10 ppb in 2006, and the maximum permissible level or threshold level value (TLV-value) at any given time is 0.2 mg/m^3. Tables 1.1 and 1.2 show the quality of copper concentrates as a function of arsenic content and the maximum contaminant level in drinking water, concentration in air and aqueous effluents (Castro 2008).

Table 1.1 Quality of copper concentrates as a function of arsenic content (Castro 2008)

Arsenic content (wt. %)	Arsenic impurity level
<0.010	Very low
0.01 – 0.1	Low
0.1 – 0.3	Moderate
0.3 – 1.0	High
1.0 – 2.0	Very high
>2.0	Requires pre-treatment

Table 1.2: Environmental regulations for arsenic emissions in some countries (Castro 2008)

Country	Drinking water (ppb)	Air (mg/Nm3)	Aqueous Effluents (ppb)
Peru	100	25	300
Chile	50	--	200
Australia	7.0	1.0	700
U.S.A.	10	0.5	1000
South Africa	50	0.1	20
Germany	40	1.0	100
Canada	25	--	--

Chapter 2 Objectives

The present work has set as its objectives the following:

1. To study the selective leaching of arsenic and antimony from enargite using sodium hydroxide and sodium sulphide and confirm previous findings by different authors.

2. To provide a literature review and an experimental procedure that allows a better understanding of the Cu-As-Sb-S-H_2O system.

3. To study the possibility of using minerals such as chalcopyrite and/or pyrite to produce sodium sulphide in situ.

4. To study feasible ways of removing arsenic and antimony from solution without consuming the free sulphide ions.

5. To provide useful information in regards to a practical application of the leaching procedure. Special attention will be given to the behaviour of the slurry at high pulp densities and high reagent dosage and their effect on filtration or further process steps.

Chapter 3 Literature review

3.1 Copper, arsenic and antimony overview

Copper was the first metal used by humans, it is usually of red-orange colour, ductile and malleable and is used in alloys such as bronze and brass. Its main properties are high heat and electrical conductivity, which makes its primary use in electrical applications (wires). Other applications of copper include piping, biomedical, architectural, etc.

Copper is mainly mined from sulphide ores, chalcopyrite being the most common of them. Usually sulphides are crushed, ground, floated and smelted before undergoing more refining steps. However, oxide ores have also become relevant (especially after the development of solvent extraction technologies), and in this case the ores are usually leached in heaps, filtered. The PLS is purified to then undergo electro-winning to recover the copper from solution (Davenport 2002).

COPPER PRICE
Sep 7, 2010 - Mar 3, 2011

Figure 3.1: Copper price between September 2010 and February 2011

(http://www.infomine.com)

COPPER PRICE
Mar 9, 2001 - Feb 25, 2011
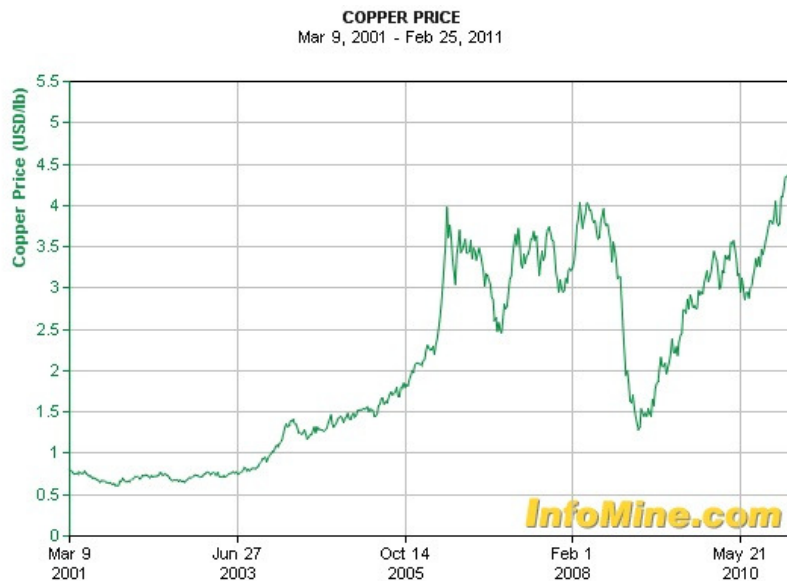
Figure 3.2: Copper price in the last ten years (http://www.infomine.com)

Copper production in the year 2008 was approximately 15 million metric tonnes, with Chile being the main producer at approximately 5 million tonnes. Copper price has shown a more or less steady increase in the last 10 years, with the exception of 2008 and 2009, and has reached a price of over 4 US$/lb at the end of 2010. The main producers of

arsenic are China, Chile and Peru (www.infomine.com, London Metal Exchange website, Mandal 2002).

Arsenic is a metalloid that can be found in nature often associated with sulphur and metals, such as copper. Arsenic is a toxic material, and this property has made it useful as a wood preservative and as an insecticide and in warfare as a chemical weapon. Arsenic is also used in some alloys used in some types of batteries and semiconductors. Other uses include pigments, food and medicine. Even though arsenic has some useful properties, its toxicity makes it undesirable in most cases and its use is constantly decreasing (Mandal 2002). Antimony, like arsenic, is a metalloid found in nature associated with sulphur and other metals. Some of its applications include flame retardants, alloys (batteries), microelectrics and medicine. Similarly to arsenic, antimony is toxic, which narrows its applications. It can cause cancer, kidney failure or even death. Arsenic and antimony share many properties including toxicity and mobility in aqueous systems. This, and their association with copper, gold and silver ores make the development of stabilization technologies an urgent matter for researchers and mining companies (Mandal 2002).

3.2 Processing of copper sulphides containing arsenic

Traditionally copper sulphides are treated via comminution, froth flotation and pyrometallurgical processes. If considerable amounts of arsenic reach the pyrometallurgy part of the process technical issues may appear. If arsenic ends up in the final copper product it will hinder its quality; therefore it would be desirable to remove arsenic before it reaches the smelting operation.

In the flotation stage the copper sulphide phases are separated from gangue minerals (oxides and silica), and in fact enargite can be floated together with chalcopyrite for example. Enargite has shown good floatability even with low concentrations of collectors, unfortunately, selective separation of enargite from other "clean" copper

sulphides seems more difficult (Castro 2008, Ma 2009). In order to achieve selective separation of enargite from other copper sulphides, several authors have performed very careful studies of the surface chemistry of enargite, effect of pH, Eh, pulp density, etc. (Castro 2005, Fullston 1999, Fornasiero 2001, Guo 2002, Guo 2005, Senior 2006). In general the authors agree that under very specific conditions it is possible to selectively float enargite from other copper sulphides; however, the high copper content and the common presence of precious metals in enargite, make it attractive to develop processes capable of treating ores high in arsenic .

3.2.1 Arsenic in pyrometallurgical operations

3.2.1.1 Roasting

Enargite is known to decompose quickly at temperatures above 500°C. In a non-oxidizing atmosphere gaseous arsenic sulphides will form, and as oxygen partial pressure is increased gaseous arsenic oxides will form and will be removed from the concentrate (Valenzuela 2000, Wilkomirsky 2010). Care must be taken when oxidizing the gaseous arsenic sulphide, because arsenic (III) oxide is more desirable since arsenic (V) oxide has a higher evaporation temperature (Valenzuela 2000). The nature of these reactions is complex and can happen in several stages depending on conditions such as temperature and type of gas used (Nakazawa 1999, Valenzuela 2000)

The roasting process can be undertaken in a multiple hearth furnace like at El Indio operation in Chile or in a fluidized bed reactor like at Lepanto in the Philippines (Valenzuela 2000). However, fluidized bed reactors present several advantages over multiple hearth furnaces; fluidized beds present considerably less moving parts, which decreases maintenance and the energy efficiency is also higher in part due to the much better mixing found in a fluidized bed (Lindkvist 1983). The output gases rich in arsenic

are treated and arsenic trioxide is precipitated, which is later disposed or, preferably, treated via hydrometallurgy.

3.2.1.2 Smelting

It is known that arsenic can be volatilized at high temperatures (Padilla 2001). Roasting operations take advantage of this property and as mentioned above, these are used to remove arsenic making the material suitable for leaching or smelting.

One could think that, since smelting of copper sulphides occurs at a higher temperature than roasting (approximately 1300°C compared to approximately 750°C), the removal of arsenic would be more efficient. However there are several factors that make the pre-treatment of arsenic bearing concentrates necessary before undergoing smelting. In general, the reaction time in smelters (contact between gas and solid) is much faster than in roasters, especially in flash smelting. Arsenic also has a high solubility in metallic copper; therefore entrapment occurs and increases when metallic copper content increases in the matte, for example. In the case of flash smelting there can be large amounts of dust in the reactor that contain arsenic, and when in contact with the molten bath entrapment could also take place (Itagaki 1983, Dabbs 1983, Biswas 1994, Valenzuela 2000, Wilkomirsky 2010).

In general, smelting operations can have arsenic removals as low as 50 %. Wilkomirsky *et al* (Wilkomirsky 2008-2010) have developed a new reactor capable of treating high arsenic concentrates (2.6 % As) and produce white metal with 75 to 78 % of copper removing up to 96 % of the arsenic. Their idea was to build a reactor in which the reactions occur in a molten layer around its walls and operate it a higher temperatures up to 1650°C.

So far direct smelting of arsenic bearing concentrates does not seem to have been tested with arsenic contents above 3 %. Even though sulphide smelting is a proven,

efficient technology, high arsenic deposits are becoming more common, like the Tampakan deposit in the Philippines and MMH in Chile (Baxter 2010, Wilkomirsky 2010), and smelting does not seem to be able to handle such ores. Therefore pre-treatment routes will very likely be necessary, and even though roasting has proven to be the first choice in several cases (El Indio, Lepanto, MMH) having volatile arsenic may not be desirable, regardless of how efficient the gas treatment process can be. This opens a gap of opportunity for hydrometallurgical treatments, especially something like the sodium sulphide leach that could be followed by a smelting step.

3.2.1.3 Treatment of smelter flue gas

One common source of arsenic is smelter or roaster flue gas. After arsenic is volatilized and precipitated preferably as arsenic trioxide, it can be disposed as a hazardous material or treated to form a more suitable compound for disposal.

In general, treatment of arsenic trioxide coming from pyrometallurgical operations could consists of an acid leach step (Ke 2000, Zhang 1988, Madsen 1983, Reynolds 1981, Ferron 2000, Viñals 2010), or an alkaline leach step (Zhang 1988, Robles 1999), or a pyrometallurgical step that consists on encapsulating the arsenic in the slag (Twidell 1985, Coursol 2006).

The most common alternative for treatment of arsenic bearing flue dust seems to be acid leach followed by precipitation with lime or ferric ions. However the nature of the process and final arsenic disposal method will change considerably depending on the operation, characteristics of the ore, environmental regulations and even the weather conditions of the location.

3.2.2 Hydrometallurgical processing of enargite

3.2.2.1 Acid leaching

Enargite has proven to be refractory to acid leaching. For many years researchers have studied the leaching behaviour of enargite in acid solutions (Dutrizac 1972, Flynn 1989, Hourn 1999, Dreisinger 1999, Padilla 2005, Riveros 2008, Padilla 2008, Rivera 2009). In most cases the preferred lixiviant is sulphuric acid, using ferric ions as oxidant to release copper and arsenic into solution and produce elemental sulphur, as shown in Equation 3.2.1 (Dutrizac 1972). Also, oxygen has been used as the main oxidant of enargite during acid leach under high pressure, as shown in Equation 3.2.2 (Padilla 2005). In some cases chloride ions are added to increase dissolution rates (Riveros 2001, Padilla 2005) or chloride media itself is used (Herreros 2002, Mayhew 2010)

$$Cu_3AsS_4 + 11Fe^{3+} + 4H_2O \Leftrightarrow 3Cu^{2+} + AsO_4^{3-} + 4S^0 + 11Fe^{2+} + 8H^+ \qquad 3.2.1$$

$$2Cu_3AsS_4 + 5H_2SO_4 + 7O_2 \Leftrightarrow 6CuSO_4 + 2H_3AsO_4 + 7S^0 + 2H_2O \qquad 3.2.2$$
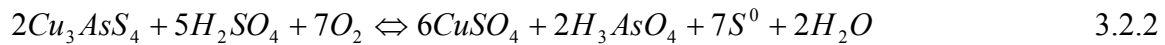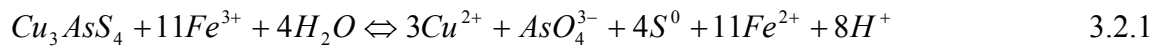
In general, enargite will dissolve in acidic solutions only at high temperatures and pressures of up to 220°C and 7 atm. (Dreisinger 1999, Padilla 2005). Under atmospheric conditions the dissolution rate of enargite is slow. Padilla *et al* (Padilla 2005) reports that at 100°C only 6 % of the arsenic is dissolved in 7 h.

Dissolution of enargite under atmospheric conditions has been achieved by fine grinding; p80 of 20 μm or finer (ALBION process, Hourn 1999) or by using pyrite as a catalyst like in the Galvanox[TM] process (Rivera 2009).

High pressure leaching of arsenic can have high costs but it has found application in the processing of refractory gold ores and fine grinding yields good extractions but fine grinding can also be costly. Ideally a process like Galvanox[TM] which uses atmospheric

conditions would be more desirable if acid leaching of enargite is the chosen processing route.

3.2.2.2 Alkaline leaching of enargite

The alkaline leaching of enargite in ammoniacal solutions has been reported by Gajam (Gajam 1982) and results indicate that enargite is one of the most refractory copper sulphides to the ammonia leach reaching only 60 % of copper extraction after 24 hours in the case of Gajam's work.

Another approach is the alkaline leaching of enargite using sodium hypochlorite (Viñals 2003, Curreli 2005, Mihajlovic 2007, Musu 2009). In this case leaching is selective for arsenic and enargite decomposes to form copper oxides and soluble sodium arsenate. The change from enargite to copper oxide is described as a topochemical reaction (Viñals 2003).

The alkaline leaching of enargite using hypochlorite is reported to occur as follows (Viñals 2003):

$$
\begin{aligned}
& 2Cu_3AsS_{4(s)} + 22OH^-_{(aq)} + 35ClO^-_{(aq)} \Leftrightarrow \\
& 6CuO_{(s)} + 2AsO^{3-}_{4(aq)} + 8SO^{2-}_{4(aq)} + 11H_2O_{(l)} + 35Cl^-_{(aq)}
\end{aligned}
\qquad 3.2.3
$$
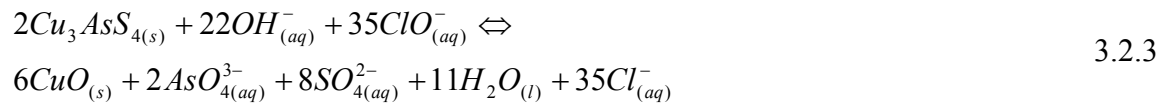
The alkaline leaching of enargite using sodium hypochlorite has been reported to have fast kinetics, reaching total removal of arsenic in less than one hour at 60ºC (Viñals 2003), however it seems to be subject to high reagent cost and has not been used at the industrial scale.

3.3 Arsenic removal from solution and final disposal options

Aqueous arsenic is a common issue in metallurgical operations. Its removal must be done in such way that the final concentration in the streams is approved by regulatory agencies and the disposed arsenic bearing residues are stable in the long term. The United States Environmental Protection Agency (EPA) fixed the maximum amount of arsenic in drinking water at 10 ppb, whereas Canada maintains a limit of 25 ppb (Riveros 2001, Castro 2008).

Although it is difficult to determine the stability of arsenic bearing compounds in the long term, the EPA has developed the Toxicity Characteristic Leaching Procedure (TCLP) which has been adopted by the mining industry. The TCLP consists of mixing a solid with a known volume of pH 5 buffered acetic acid solution followed by the measurement of dissolved element concentrations after 20 hours (Riveros 2001).

Even though the TCLP is used to validate an arsenic bearing residue as suitable for disposal, it is only applicable to short term stability studies. The long term stability of arsenic compounds depends on several factors such as disposal site characteristics (humidity, rain fall), crystallinity, presence of oxygen, sulphides and complexing agents (Riveros 2001)

Arsenic removal processes have been reviewed by Twidell *et al* (Twidell 1999) and Riveros *et al* (Riveros 2001) and are summarized in Table 3.1

Table 3.1: Arsenic removal processes (Twidell 1999)

Precipitation	Calcium Arsenates
	Mineral-like arsenates
	Iron Arsenates
Adsorption	Ferrihydrite
	Aluminum hydroxide
	Alumina
	Activated Carbon
	Other Sorbents
Ion Exchange / Reverse Osmosis	Ion Exchange
	Liquid ion exchange
	Reverse osmosis
Cementation	Iron cementation

3.3.1 Arsenic removal by lime precipitation

Precipitation of arsenic with lime is still practiced in several operations despite its long term stability problems. Arsenic is precipitated as calcium arsenate compounds from solution in the presence of lime. Table 3.2 shows calcium arsenate compounds found by some authors (Bothe 1999, Swash 1995). Calcium arsenates are known for being unstable in the long term. They react with carbon dioxide and moisture from the environment and form calcium carbonate and release soluble arsenic. In some areas where the climate is extremely dry (like northern Chile), disposal of calcium arsenates may be acceptable, however, in most places, this procedure is being replaced (Riveros 2001).

Table 3.2: Calcium arsenates reported by Bothe (1999) and Swash (1995)

Bothe *et al* (1999)	$Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$
	$Ca_5(AsO_4)_3OH$
	$Ca_3(AsO_4)_2 \cdot 32/3H_2O$
Swash *et al* (1995)	$CaHAsO_4 \cdot xH_2O$
	$Ca_5H_2(AsO_4)_4$

Equation 3.3.1 shows how calcium arsenates can react with carbon dioxide to release arsenic acid (Riveros 2001).

$$Ca_3(AsO_4)_{2(s)} + 3CO_{2(g)} + 3H_2O_{(l)} \Leftrightarrow 3CaCO_{3(s)} + 2H_3AsO_{4(aq)} \hspace{3cm} 3.3.1$$
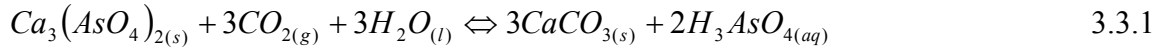
In regards to the stability of calcium arsenates, Swash *et al* (Swash 1995) synthesized several calcium arsenates under different conditions and found that none of them passed the EPA TCLP test. The arsenic concentrations reached levels as high as 4400 ppm.

Table 3.3: TCLP results on calcium arsenates (Monhemius 1999)

Precipitated phase		TCLP Solubility (As in ppm)
Calcium arsenates	Guerinite	>1000
	Weilite	>2000
	Haidingerite	>3000
	Pharmacolite	>3000

An additional step to enhance the stability of calcium arsenates is to calcine them at 700°C or more. This leads to the generation of crystalline calcium arsenates, which are less soluble than their amorphous versions. In some cases they pass the EPA TCLP test. It has been reported that no arsenic is volatilized and that arsenite is oxidised to arsenate, thus, it is not necessary to oxidise the arsenite prior to the lime precipitation. However, other authors have reported that arsenites do not oxidise completely at temperatures below 800°C (Riveros 2001). Even though the solubility of calcined calcium arsenates is lower than non calcined arsenates, there is a chance that in the long term they will become unstable and release arsenic into the environment once the buffering effect of the excess lime is reduced. Several Chilean operations apply the calcination process to their calcium arsenates without reporting any problems; however, they are located in the driest place in the world (Swash 1995).

3.3.2 Co-precipitation of arsenic using ferric ions (ferrihydrite process)

Ferrihydrite is a polycrystalline ferric oxyhydroxide phase. It has a large surface area (200 m^2/g) (Zhao 1994) which makes it suitable for adsoprtion of ions. The EPA has designated the co-precipitation of arsenic with ferric ions as the "best demonstrated available technology" (BDAT) (Riveros 2001). This process works best in a pH range of 4 to 7 (Robins 1988), but the presence of other metal ions like Zn^{2+}, Cd^{2+}, Pb^{2+}, Ca^{2+} and Mg^{2+} can increase that range to 4 to 9 (Riveros 2001). The co-precipitation has been reported to work better with arsenic (V) rather than arsenic (III) (Nishimura 2000). Sulphate ions and silicic acid have been reported to decrease the arsenic removal. Sulphate ions will compete for sites in the ferrihydrite network (Krause 1989, Swelund 1999) and so will silicic acid. Also, silicic acid will decrease arsenic adsorption due to polymerisation, but to a lesser extent than adsoprtion. A similar effect has been seen on goethite when used as an agent for arsenic adsorption (Waltman 2002).

The ferrihydrite process passes the TCLP test and has proven to be a stable residue for periods of at least one year. Several operations use this process but its nanocrystalline, hydrated and voluminous nature are some of its drawbacks (Riveros 2001, Zhao 1994, Swedlund 1999)

3.3.3 Scorodite precipitation

This process is performed in autoclaves at temperatures between 150 to 230°C. In the presence of dissolved arsenic, ferric sulphate is added and ferric arsenate is precipitated. Under autoclave conditions the precipitate is similar to natural scorodite; it has good settling properties, low water retention and is less voluminous than ferrihydrite (Riveros 2001, Zhao 1994). Besides scorodite, two other phases have been identified, Type I and Type 2 (Swash 1995). The authors indicate that only Type I does not pass the TCLP test. The main application for this process is found in the processing of gold ores,

where roasting and volatilization of the arsenic was the main arsenic removal method used. Its advantages over roasting include elimination of gaseous and particulate arsenic compounds emissions to the atmosphere, sulphur dioxide emissions, elimination of underground storage for arsenic trioxide, reduction of arsenic and heavy metals in aqueous effluents and increased gold recoveries (Riveros 2001, Filippou 1997, Langmuir 2006).

The nature of the ferric arsenate precipitate and the conditions under which it is produced (like pH and temperature) will depend on several factors. The source of arsenic, the amount of arsenic in solution, medium used (sulphate, nitrate, chloride), initial iron concentration are some of these factors (Riveros 2001, Dutrizac 1988, Demopoulos 1989, Papangelakis 1990, Monhemius 1999, Papassiopi 1996)

Even though scorodite precipitation has been extensively studied in autoclaves, there are studies that show it can be produced at temperatures below 100°C. Demopoulos *et al* (Demopoulos 1995), Shalabh *et al* (Shalabh 2005) have performed studies on atmospheric precipitation of scorodite from chloride and sulphate solutions and the effect of seeding with crystalline hydrothermally produced scorodite. Also, Fujita *et al* studied the atmospheric precipitation of scorodite form sulphate solutions and tested its physical properties and stability (Fujita 2008 - 2009).

Table 3.3 shows scorodite and mineral type I and II formulae and TCLP results according to Swash and Monhemius (Swash 1995, Monhemius 1999)

Table 3.4: Ferric arsenate formulae and TCLP solubility (Swash 1995, Monhemius 1999)

Compound	Formula	TCLP Solubility (As in ppm)
Scorodite	$FeAsO_4 \cdot H_2O$	<5
Type I	$Fe_2(HAsO_4)_3 \cdot xH_2O$ x < 4	5-85
Type II	$Fe_4(AsO_4)_3(OH)_x(SO_4)_y$ x + 2y = 3	<5

Scorodite seems to be an attractive alternative for safe arsenic disposal. It is a compact, easy to filter solid, which complies with the EPA TCLP requirements. In the case of refractory arsenic bearing gold ores, it enhances gold recoveries and eliminates emissions of gaseous arsenates. Even though its solubility product has been reported to be in the order of 10^{-25} (Bluteau 2007, Langmuir 2006), it has been reported that scorodite is metastable under most conditions, including atmospheric (Welham 2000). Also, iron (III) and arsenic (V) can be reduced to soluble arsenic (III) by sulphides, especially when storing arsenic residues under water. After 2 meters of depth, environments can become anaerobic, increasing the activity of sulphides (Hopkin 1989). Stichbury *et al* (Stichbury 2000) have also seen reduction and dissolution of arsenic by bacterial activity.

It seems that safe final disposal of arsenic cannot be guaranteed based on the nature of even the most stable known (and feasible to produce) arsenic compounds. Perhaps materials and local conditions (such as weather) where arsenic is being disposed would help to ensure that arsenic will not be released into the environment in the future.

3.3.4 Alternatives to remove arsenic from alkaline sodium sulphide solutions

3.3.4.1 Precipitation by cooling

In alkaline sodium sulphide solutions, arsenic is reported to exist as arsenic (V) in the form of thioarsenate (AsS_4^{3-}) (Stauder 2005), and in some cases it has been reported that it can exist as arsenic (III) in the form of thioarsenite (AsS_3^{3-}) (Edwards 1985, Ackerman 1993). The solubility curves of sodium thioarsenate have been reported to be "steep", making it suitable for precipitation by cooling (Nadkarni 1988). Solubility curves developed by Nadkarni show that at 40°C sodium thioarsenate has a solubility of approximately 0.5 M and decreases to 0.09 M at 20°C. Supporting Nadkarni's results, other authors have also reported that cooling can be used to crystallize sodium

thioarsenate (Coltrinari 1977). However, Coltrinari states that arsenic (and antimony) must be in the 5+ state in order to precipitate by cooling or evaporation or a mixture of both techniques; arsenic would be dissolved as arsenic (V) when coming from enargite, or other mineral containing arsenic (V), and the same situation would apply when a mineral contains arsenic (III) like orpiment (As_2S_3). In the Equity Leach Plant (Edwards 1985) it has been reported that arsenic (III) coming from tennantite leaches as thioarsenate, in accordance with Coltrinari's observations.

In order oxidise arsenite to arsenate and ensure precipitation of the sodium thioarsenate, Coltrinari suggests the addition of elemental sulphur, as shown in Equation 3.3.2.

$$Na_3AsS_{3(aq)} + S^0_{(s)} \Leftrightarrow Na_3AsS_{4(aq)} \qquad\qquad 3.3.2$$
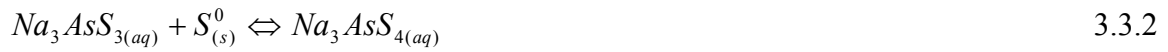
After precipitation of sodium thioarsenate and washing the precipitated crystals, they can be treated with acid to form arsenic sulphides and gaseous hydrogen sulphide (H_2S) and sodium sulphate as shown in Equation 3.3.3 (Nadkarni 1975 – 1988). The arsenic sulphides can undergo further processing to produce a suitable arsenic compound for final disposal (scorodite).

$$3H_2SO_{4(aq)} + Na_3AsS_{4(s)} \Leftrightarrow As_2S_{5(s)} + Na_2SO_{4(aq)} + 3H_2S_{(g)} \qquad\qquad 3.3.3$$
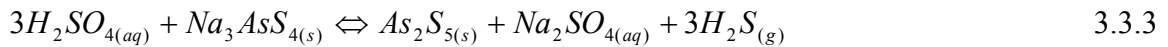
The sodium sulphate produced can be reacted with lime to precipitate gypsum and produce free sodium hydroxide. This sodium hydroxide solution can be put in contact with the hydrogen sulphide produced in Equation 3.3.3 thus regenerating sodium sulphide as proposed by Nadkarni (Nadkarni 1975).

The following reactions show how sodium sulphate and hydrogen sulphide can be used to regenerate sodium sulphide.

$$Na_2SO_{4(aq)} + Ca(OH)_2 \Leftrightarrow CaSO_{4(s)} + 2NaOH_{(aq)} \qquad\qquad 3.3.4$$

$$2NaOH_{(aq)} + H_2S_{(g)} \Leftrightarrow Na_2S_{(aq)} + 2H_2O \qquad\qquad 3.3.5$$
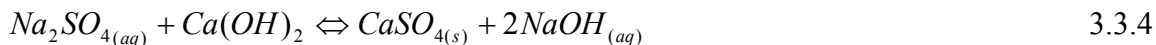
Since the removal of arsenic will depend on its solubility part of it will be recirculated, which may affect the pulp density in the leaching stage depending on the arsenic to antimony ratio of the feed. However, precipitation of sodium thioarsenate by cooling and further processing to produce scorodite and regenerate sodium sulphide and sodium hydroxide seems to be a convenient method considering that it would be a low cost alternative and that crystallizers are commonly used in the mining industry.

3.4 Alkaline sodium sulphide leaching of enargite

The alkaline sodium sulphide leach process has been developed for the removal of arsenic, antimony, mercury and tin. Initially this process was used to upgrade silver concentrates by removing antimony mainly from tetrahedrite (Holmes 1943, Raudsepp 1981, Edwards 1985, Ackerman 1993, Anderson 1994, Filippou 2007). Two well known operations that used this process are the Sunshine antimony refinery (Ackerman 1993) in Idaho, USA, and the Equity silver mine (Edwards 1985) in British Columbia, Canada. Both operations are now closed.

3.4.1 Sunshine metallurgical complex

The entire concentrate processing of scheme at the Sunshine mine was hydrometallurgical. It began as an antimony refinery during World War II that used sodium sulphide alkaline leaching of the antimony, and later it added a silver-copper refinery that used the nitrogen species catalyzed sulphuric acid pressure leach system (Ackerman 1993).

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Table 3.5 shows the main elements found in the concentrate prior to the alkaline leach. Copper, silver and antimony are associated mostly to tetrahedrite and the other elements to pyrite, arsenopyrite, siderite, sphalerite and galena.

Table 3.5: Sunshine antimony leach plant feed

Element	Content (%)
Ag	4.5
Cu	20
Sb	19
Fe	18
As	2.0
Pb	2.0
Zn	2.0
S	28

The alkaline leach was carried out at 104ºC at atmospheric pressure. The leach solution was produced by adding elemental sulphur to a sodium hydroxide solution. This led to the production of sodium sulphide but also to polysulphides and thiosulphates. However, most of the solution was recirculated and thus it was already rich in sodium sulphide; therefore the elemental sulphur added will tend to generate sodium sulphide, which is stable at more reducing potentials compared with thiosulphates and polysulphides. These reactions are shown in reactions 3.4.1 and 3.4.2.

$$4S_{(s)} + 6NaOH_{(aq)} \Rightarrow 2Na_2S_{(aq)} + Na_2S_2O_{3(aq)} + 3H_2O \qquad\qquad 3.4.1$$

$$(x-1)S_{(s)} + Na_2S_{(aq)} \Rightarrow Na_2S_{x(aq)} \quad (x = 2 \text{ to } 5) \qquad\qquad 3.4.2$$
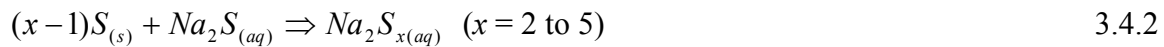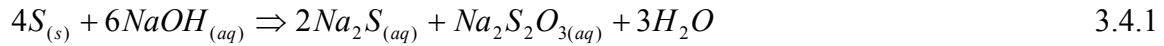
The leached antimony was later electrowon or precipitated as sodium antimonate and then sold. The sodium antimonate is produced by oxidation with oxygen and recovered by settling. The arsenic remains in solution as sodium arsenate and is then precipitated as ferrous arsenate at pH 7 to 8.

In the antimony electrowinning step, sulphur species compete with the main cathodic reaction and sulphide is produced. Thus, the spent electrolyte can be recirculated to the leach process free of antimony and containing some sodium sulphide.

Some issues with this process included problems in the solid liquid separation after the alkaline leach due to the viscous nature of the solution and fine particle size of the concentrate. This was solved by diluting the solution and settling of the dense concentrate particles. Also, due to the many impurities found in the solution, current efficiencies in the electrowinning stage could be as low as 30 % even in a diaphragm cell. This problem was solved by means of solution purification which allowed the current efficiency to rise up to 75 % in a diaphragmless cell.

3.4.2 The equity leach plant

The Equity mine was the largest silver mine in Canada. It produced a copper concentrate with high concentrations of silver and gold. Its mineralogy consisted of high antimony and arsenic grade minerals like tetrahedrite and tennantite. Pyrite, chalcopyrite and arsenopyrite were also commonly found in the deposit. Table 3.6 shows the main mineralogical phases found in the ore and concentrate (Edwards 1985).

Table 3.6: Major minerals in the equity plant concentrate

Major concentrate minerals	
Tetrahedrite	$Cu_{12}Sb_4S_{13}$
Tennantite	$Cu_{12}As_4S_{13}$
Chalcopyrite	$CuFeS_2$
Pyrite	FeS_2
Sphalerite	ZnS
Galena	PbS
Arsenopyrite	$FeAsS$

The high content of antimony and arsenic in the concentrate was subject to high penalties from smelters (up to 8 % antimony and 5 % arsenic), therefore an antimony and arsenic removal process was necessary. The alkaline sulphide leach process used by Sunshine Mining was considered. The objective was to produce a "clean" concentrate containing 0.3 % antimony and 0.8 % arsenic or less.

In order to achieve suitable impurity levels in the upgraded concentrate, the sodium hydroxide – sodium sulphide leach was run at 107ºC for eight hours. However, several problems were encountered. Reagent dosage was not reliable, which led to low reagent concentrations and logically poor antimony and arsenic removal. Also, the presence of arsenopyrite, which is refractory to the alkaline leach, increased the amount of arsenic in the residue. Analyzing insoluble arsenic in the feed was too complex due to a time consuming analysis method and fluctuating arsenopyrite content in the concentrate. The subsequent stages of the process also presented several challenges. Blowing filter cakes with air caused excessive heat due to partial oxidation of the concentrate, so nitrogen was used instead.

Removal of antimony from solution was done in autoclaves under oxygen atmosphere, to selectively precipitate sodium antimonate, but difficult control of dissolved oxygen led to antimony recoveries of only 80 %. Oxidation of arsenic and precipitation as calcium arsenate was also done in autoclaves. Arsenic was removed down to a final concentration of 20 ppm, which was necessary for the production of saleable sodium sulphate. A sodium concentration of less than 80 g/l in the autoclave feed helped meet the desired arsenic precipitation performance.

One interesting fact about Sunshine and Equity operations, is that both state that after the sodium sulphide leach, antimony stays in the 3+ state and due to the effect of polysulphides it can be oxidized to the +5 state, and, in the case of the Equity leach both, antimony and arsenic are found in the 3+ state, unlike the rest of the literature that states both should be found in the +5 state (Anderson 2008, Curreli 2009, Tongamp 2009).

In fact, an article on arsenate reduction by dissolved sulphide by Rochette *et al* (Rochette 2000) states that reduction of arsenic V to arsenic III is very pH dependant and occurs faster at slightly acidic pH (pH ~ 4). At pH 7 it occurs 300 times slower and it is expected to occur even slower at higher pH, like that found in the alkaline sodium sulphide leach solution (pH > 12). One important fact is that Rochette *et al* state that the reduction of the arsenic (V) to arsenic (III) leads to the precipitation of an arsenic sulphide similar to orpiment (As_2S_3), which provides a possibility of arsenic removal from the leach solution.

The Equity and the Sunshine operations are interesting examples that show the alkaline leach of antimony and arsenic can be performed in large scale. There are some difficulties that are particular to this process, however, it can efficiently remove antimony and arsenic and, according to Baxter *et al* (Baxter 2010), this process is being considered to treat a part of the concentrate produced in the Tampakan deposit in the Philippines.

3.4.3 Sodium sulphide alkaline leach process applied to enargite concentrates

The alkaline sodium sulphide leach process was later adopted for the removal of arsenic from copper sulphide ores (Holmes 1973, Nadkarni 1975, Coltriari 1977, Carly 1980). Literature usually refers to enargite as the main arsenic source, but also minerals such as tennantite and luzonite are considered (Filippou 2007). Only arsenopyrite, which is not a copper source, has been reported to be refractory to the alkaline sulphide leach (Edwards 1985).

The alkaline sodium sulphide leach process works at atmospheric conditions at temperatures between 80 to 110ºC (Filippou 2007) just below the boiling point of a sodium hydroxide − sodium sulphide solution. Arsenic is released from the enargite forming sodium thioarsenate as shown by the next reaction:

$$2Cu_3AsS_{4(s)} + 3Na_2S_{(aq)} \Rightarrow 3Cu_2S(s) + 2Na_3AsS_{4(aq)} \qquad\qquad 3.4.3$$
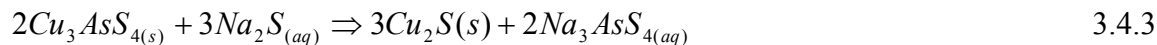
It has been reported that in order to ensure the presence of sulphide ions, enough caustic must be added to avoid hydrolization to hydrosulphide ions (Holmes 1973, Nadkarni 1975-1988, Coltriari 1977, Carly 1980, Anderson 2008, Curreli 2009), which is thought to decrease leaching performance. Ideally the solution pH should be maintained above 12, which is approximately were sulphide ions exist (Anderson 2008), as shown in Figure 3.3.
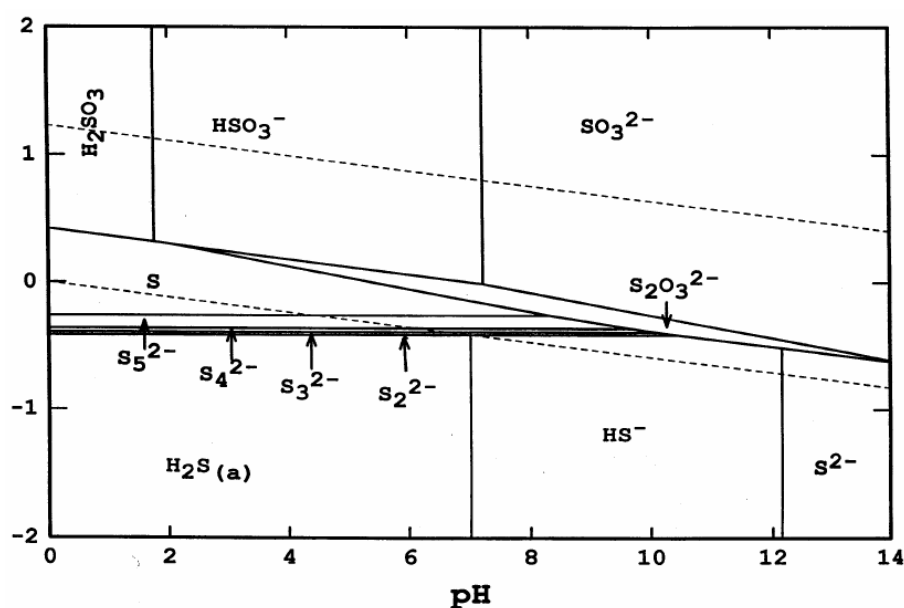
Figure 3.3: Meta-stable S-H$_2$O Eh pH diagram (Anderson 2008)

However, other researchers have reported that the free energy of formation for aqueous sulphide is approximately 111 kJ/mol, which means the second dissociation constant of H$_2$S is approximately 10^{-17}, which suggests that sulphide ions would predominate only at a pH 17 or greater (Giggenbach 1971, Licht 1988, Protopopoff 2003). Therefore, it can be said that in reality there is a predominance of hydrosulphide ions rather than sulphide, even at pH greater than 12, as shown in Figure 3.4, which may provide the option of leaching with less caustic.

$$H_2S \Rightarrow HS^- + H^+ \qquad\qquad pK_1 \approx 7 \qquad\qquad 3.4.4$$

$$HS^- \Rightarrow S^{2-} + H^+ \qquad\qquad pK_2 \approx 17 \qquad\qquad 3.4.5$$
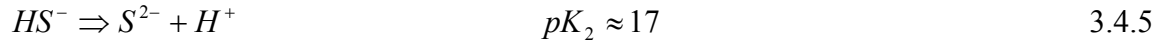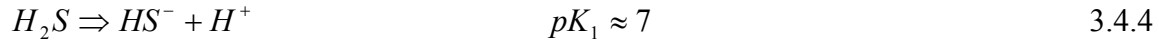
Considering this newly proposed predominance area for hydrosulphide, in reality what is likely occurring is the hydrosulphide leaching of enargite, as shown in Equation 3.4.6 (Tongamp, 2009, 2010)

$$2Cu_3AsS_{4(s)} + 3NaHS_{(aq)} + 3NaOH_{(aq)} \Rightarrow 3Cu_2S_{(s)} + 3H_2O_{(l)} + 2Na_3AsS_{4(aq)} \qquad 3.4.6$$
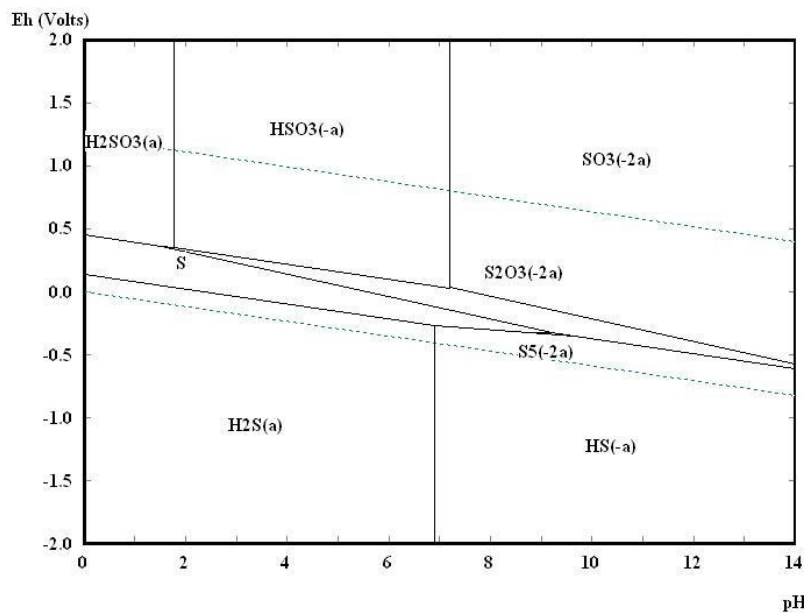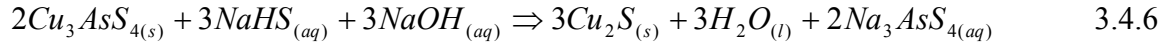
Figure 3.4: Meta-stable S-H$_2$O Eh pH diagram at 25°C (HSC software)

Nonetheless, all researchers agree that at higher pH removal of arsenic is faster, and their results support this conclusion. Similarly, increasing the concentration of sodium sulphide will increase arsenic recovery (Nadkarni 1988, Anderson 2008, Curreli 2009, Tongamp 2009-2010). However, Delfini *et al* (Delfini 2003), show that better results were obtained at pH 12 rather than 13, while keeping all other conditions constant. There is no further explanation for this result, although they did not work with enargite, but with arsenic bearing borogypsum.

In general researchers agree that increasing sodium hydroxide and sodium sulphide concentrations increases arsenic leaching rates (Nadkarni 1988, Anderson 2008, Curreli 2009, Tongamp 2009-2010). However, corrosion issues brought by caustic conditions and the high price of the sodium sulphide make it desirable to optimize their dosage. Some of the main conditions and results found by these researchers are shown in Tables 3.7 to 3.12.

Despite the agreement that higher concentrations will produce higher arsenic extractions, there are some differences as to what the optimum conditions are. Nadkarni *et al* (Nadkarni 1988) mention that a sodium hydroxide concentration of 0.25 molar was enough to reach an arsenic removal of 90 %, while having a sodium sulphide concentration equivalent to twice the stoichiometric amount given by Equation 3.4.3, in their case 2.5 molar. The authors do not provide information on the particle size of the leach material.

Curreli *et al* (Curreli 2009) show results obtained after leaching enargite bearing core samples from the Serrenti-Furtei gold deposit in Sardinia, Italy. The authors report that best results are obtained when using concentrations of 2.5 molar NaOH and 0.42 molar Na_2S, or 3.75 molar NaOH and 0.21 molar Na_2S. They reach arsenic extractions of over 90 % in 2 hours with a particle size of 20 microns (P_{100}); however they used a very low solid content in the slurry, 5 grams of mineral per 500 g of leach solution.

Table 3.7: Feed assay, Curreli *et al* (Curreli 2009)

Feed Assay	
Au (ppb)	90.25
Cu (%)	33.15
As (%)	12.55
Fe (%)	9.160

Table 3.8: Effect of temperature results by Curreli *et al* (Curreli 2009)

Temperature (ºC)	As removed (%)
85	50
95	70
105	> 90
115	~100

Anderson *et al* (Anderson 2008) tested the alkaline sulphide leach for the removal of arsenic, antimony, mercury and tin. Arsenic was leached from copper enargite concentrate samples with an arsenic content of 10.7 %. They reached an arsenic removal of 99.2 % and an antimony removal of 99.7 %. The conditions under which they worked are similar to other researchers, however, their leaching time was only one hour, but using a much higher solids content in the slurry compared to Curreli.

Table 3.9: Summary of leaching results by Anderson *et al* (Anderson 2008)

Feed Assay		% of metal leached	
Cu	30.1	**Cu**	0.00
As	10.7	**As**	99.2
Sb	1.20	**Sb**	99.7
Au	35.1	**Au**	14.3

Finally, Tongamp *et al* (Tongamp 2009-2010), took a different approach. They leached enargite using sodium hydrosulphide (NaHS) instead of sodium sulphide (Na_2S) at 80ºC and achieved an arsenic content of less than 0.5 % in the solid residue in 1 to 6 hours, depending on the arsenic content of the sample. Also, they show a relationship between sulphide and the arsenic content of the sample as shown on Table 3.11. However, they mention that the sample with the highest arsenic content requires the smallest sulphide to arsenic ratio. There is no further explanation for this point, but it could be due to the different mineralogy of the sample. Tongamp *et al* (Tongamp 2010) also published a kinetic study of the alkaline leaching of enargite, where they tested the effect of temperature, agitation speed, pulp density and reagent dosage and found the rate controlling mechanism was product layer diffusion. To support their findings they show an activation energy value of 70.26 kJ/mol ± 4.74 kJ/mol. Table 3.12 shows some general

conditions used by different researchers on the alkaline leaching of enargite. However, this activation energy value is considered to be chemical control by other authors.

Table 3.10: Samples used by Tongamp *et al* (Tongamp 2009)

Sample	As (%)	Cu (%)	Fe (%)	Main phases
(1) Cu conc.	0.81	26.62	25.4	$CuFeS_2$, FeS_2
(2) Cu conc.	0.95	22.60	18.17	$CuFeS_2$, FeS_2
(3) Cu conc.	1.67	11.49	9.710	$CuFeS_2$, FeS_2
(4) Cu conc.	3.11	33.46	14.34	FeS_2, Cu_2FeSiS_4
(5) Enargite ore	8.32	33.71	16.34	Cu_3AsS_4, $CuFeS_2$
(6) Mixture (1) + (5)	3.00	25.84	21.04	------
(7) Mixture (2) + (5)	3.00	25.69	21.08	------

Table 3.11: Arsenic content and required sulphide to arsenic ratio according to Tongamp *et al* (Tongamp 2009)

Sample	As (wt. %)	S^{2-}/As Ratio
Cu Concetrate	<4	>12
Mixture	3	>6
Enargite Sample	8.32	2

As shown in Table 3.12, different authors have found different optimal conditions for the alkaline leaching of enargite. Such different results can be due to different mineralogy of their samples. However, in general, the ideal temperature for this process seems to be approximately 95 to 105ºC. Only Tongamp *et al* (Tongamp 2009) found that when using NaHS a temperature of 80ºC was sufficient to reduce the arsenic content in the residue to below the 0.5 % required by some smelters (Nadkarni 1988, Tongamp 2009).

Table 3.12: Summary of leaching conditions used by cited authors.

Author	[NaOH] (M)	[Na$_2$S] (M)	Temperature ($^{\circ}$C)	Agitation (RPM)	Particle Size (μm)	Amount of solids	Leaching time
Nadkarni 1988	0.25	0.83 - 2.5 2.9	100 - 106	NA	NA	NA	NA
Anderson 2008	0.25 (free)	1.28	105	NA	NA	25 %	1 hr
Curreli 2009	1.25 - 2.5 2.5 - 3.75	0.42 0.21	30 – 115	220	10 -150 P$_{100}$	5 g per 500 g of solution	2 hr
Tongamp 2009	1.25, 2.5, 5	0.64 - 2.56	30 - 95	500 - 750	NA	100 - 1000 grams per liter of solution	10 min - 10 hr

In terms of reagent concentration there is some disagreement. While it seems that both reagents play an important role in the performance of the process, it would be best, in terms of economics, to decrease as much as possible the amount of sodium sulphide used. Curreli *et al* (Curreli 2009) show that at 2.5 M sodium hydroxide and 0.42 M sodium sulphide the leach performance is optimal, but if sodium hydroxide is lowered to 1.25 M, and sodium sulphide maintained at 0.42 M, arsenic removal reaches only approximately 50 %. Also, as sodium hydroxide is increased to 3.75 M, the concentration of sodium sulphide can be decreased to 0.21 M, with high removal of arsenic.

Anderson *et al* (Anderson 2008) take a different approach and lower sodium hydroxide concentration to 0.25 M and increase sodium sulphide to 1.28 M. This group achieves 99.2 % of arsenic removal, and does it in only one hour of leaching. They sacrifice the more expensive reagent in order to reach high arsenic extractions in a very short time. An interesting fact about Anderson's results is that they have used a much higher content of solids in the leach compared to other authors (Curreli for example) and reached very satisfactory results. This fact is supported by Tongamp (Tongamp 2009), who leached arsenic from enargite using up to 1000 grams of solids in 1000 ml of leach solution in approximately 6 hours.

3.4.4 Nature of the solid residue

Most authors agree that the leach residue will contain almost 100 % of the initial copper in the feed and it is in the form of chalcocyte (Cu_2S) or similar copper minerals like digenite, covellite or some new form of copper sulphide like $Cu_{1.5}S$ (Nadkarni 1988, Achimovičová 1999, Filippou 2007, Anderson 2008, Curreli 2009, Tongamp 2009-2010). Chalcocyte has the advantage of being leachable in acidic conditions, like it practised at Cobre las Cruces in Spain and Sepon in Laos, therefore there is already a feasible hydrometallurgical method to treat this type of concentrate (Dreisinger 2006).

The alkaline sodium sulphide leaching of enargite seems to be an efficient process for the removal of arsenic and antimony. Extensive research has been performed by different authors and their results are more or less in agreement. Some challenges remain such as removal of arsenic from solution and its final disposal form. However, considering the fact that (a) arsenic minerals are often associated with precious metals and (b) they are difficult to treat via pyrometallurgy and (c) they can be refractory minerals in acid leach, the alkaline sodium sulphide leach presents an interesting alternative.

Chapter 4 Experimental procedures

4.1 Sample preparation

Mineral samples used included two different enargite samples from Butte, Montana and generic samples of chalcopyrite and pyrite. The samples were prepared by crushing using a laboratory cone crusher and grinding using a ring mill. The crushed ore was mixed using a 10 channel splitter, obtaining 100 gram samples which were ground at different times (10, 25, 45, 90 and 180 seconds) to achieve different particle sized which ranged from approximately 100 μm to 30 μm. Each ground sample of 100 grams was then homogenized using coning and quartering.

4.2 Atmospheric shaker leaching tests

These tests were done with the intention of using them as guidelines for the rest of the work. The shaker was capable of holding 6 beakers at a time, allowing for a large amount of data to be generated in a short period of time. In each of the 6 beakers 10 grams of "Enargite 1" sample were added into 200 ml of sodium hydroxide and sodium sulphide solutions with different concentrations. The beakers were sealed with "parafilm" and a small hole was made in order to avoid the removal of the parafilm due to expansion of the gas inside the beaker. The shaker was heated to 70ºC before placing the beakers which were left inside for 24 hours. Then the samples were filtered and washed and sent for analysis.

4.3 Atmospheric reactor leaching tests

Enargite leaching tests were conducted batch wise under atmospheric pressure in a 200 ml glass jacketed cell. Temperature was controlled using a water bath thermostat. Agitation was provided by a magnetic stirrer during tests with low pulp densities and an overhead stirrer for high pulp density tests. Tests were conducted under a nitrogen atmosphere or without any type of gas added externally. All chemicals were of analytical grade and were used as received. Leach solutions were prepared by dissolving sodium hydroxide in deionised water and later adding the sodium sulphide into the alkaline solution in order to avoid evolution of hydrogen sulphide. Samples were drawn from the leaching reactor periodically (approximately 14 ml of pulp), centrifuged and filtered and sent for analysis as taken or diluted depending on the test conditions. The remaining pulp that is not used for analysis was immediately returned to the reactor. Solution potential remained more or less constant at a value of approximately -0.5 V vs. SHE. The studied variables include dosage of sodium hydroxide and sodium sulphide, temperature, agitation and pulp density and their effect on the dissolution behaviour of arsenic, antimony, copper and gold.

Chalcopyrite and pyrite tests were also carried out under the same conditions as the enargite leaching tests, however no sodium sulphide was added since in-situ production of sulphide was hoped, as suggested in the literature (Peters 1976). Thus, leaching tests were carried out only in sodium hydroxide solutions. Leaching results presented are the result of several repeated tests averaged. The Standard deviation for the effect of reagent concentration can be seen in the appendices.

4.4 Autoclave leaching tests

Samples of 10 or 20 grams of chalcopyrite, pyrite and/or enargite were contacted with 500 ml of a 0.1 M and a 2 M sodium hydroxide solution inside an autoclave under agitation. After samples and solution were fed to the reactor, it was sealed and heated up

to 220ºC. Leaching took place from 1 to 4 hours once 220ºC were reached. During the leach test temperature and pressure were monitored and once the test was finished the autoclave was cooled down (again temperature and pressure were monitored during this procedure), pulp was filtered, solids washed and sent for ICP and XRD analyses and solutions were assayed for sulphide and ICP.

4.5 Precipitation tests

Precipitation tests can be divided into two types:

1.   Precipitation by acidification using sulphuric acid, which was performed in a 200 ml glass jacketed cell under mil agitation at 95ºC with addition of sulphuric acid until reaching different pH values (2, 3, 4, 5 and 6) producing a yellow precipitate. During these tests the slurry was filtered and solution and solid samples were sent for analysis.

2.   Crystallization of sodium thioarsenate by cooling; which was performed in the same cell under mild agitation at 25ºC. Samples were drawn periodically, filtered, diluted and sent for analysis.

4.6 Arsenic trioxide leaching

Arsenic trioxide was added to a sodium sulphide – sodium hydroxide solution at 95ºC under agitation with a magnetic stirrer and left to react during 24 hours. Only one solution and solid sample was taken at the end of the test after cooling and filtration. The filtrate solution was left to rest for another week at room temperature and was filtered again to obtain another solid and solution sample.

4.7 Analyses

In order to properly characterize the ore samples used, the leach solution, solid residues and precipitates formed, they were subject to ICP, gold, fluoride, quantitative X-Ray Diffraction (XRD, Rietveld method) and EDX analyses. Chemical analyses were done in external labs as well as XRD analyses; however SEM-EDX analyses were done in the department facilities using sample powders mounted on carbon stubs.

4.8 Ore characterization

Two samples of enargite ("Enargite 1" and "Enargite 2") were used during this work; both from Butte, Montana, with some differences in their composition, as shown in Tables 4.1 to 4.4. All percentage contents are based on weight.

"Enargite 1" sample has approximately 9.3 % As, 32 % Cu and 0.24 % Sb by. The main arsenic bearing species are enargite and tennantite, which account for approximately 54 % of the sample. Copper is divided into enargite, tennantite, chalcopyrite and bornite, with some other important phases like pyrite and silica. Finally this sample contains small amounts of galena, sphalerite, dolomite and muscovite.

"Enargite 2" sample has approximately 11.7 % As, 38 % Cu, 0.46 % Sb and 1000 ppb Au. The main arsenic bearing species are enargite and tennantite, which account for approximately 65 % of the sample. Copper is divided into enargite, tennantite and covellite. Other important phases are pyrite and, as expected, quartz.

A summary of some elements of interest and phases of both samples can be seen in Tables 4.1 and 4.2. Also two chalcopyrite samples were used together with a pyrite sample. "Chalcopyrite 1", "Chalcopyrite 2" and "Pyrite 1". Their main phases are shown in Table 4.5.

Table 4.1: Elements of interest in the "Enargite 1" head sample

Element	Content (wt. %)
As	9.30
Sb	0.24
Cu	31.9
Fe	4.66
Zn	0.3
Pb	0.76

Table 4.2: Elements of interest in the "Enargite 2" head sample

Element	Content (wt. %)
As	11.7
Sb	0.46
Cu	38.9
Au (ppb)	1021
Fe	11.3
Zn	0.32
Pb	0.13

Table 4.3: Main phases found in the "Enargite 1" and "Enargite 2" head samples

Mineral	Ideal Formula	"Enargite 1" head sample	"Enargite 2" head sample
Enargite	Cu_3AsS_4	46.0	60.4
Quartz	SiO_2	28.2	5.90
Tennatite	$(Cu,Ag,Fe,Zn)_{12}As_4S_{13}$	7.80	4.90
Covellite	CuS		3.00
Pyrite	FeS_2	6.60	25.7
Chalcopyrite	$CuFeS_2$	5.90	
Bornite	Cu_5FeS_4	2.00	
Dolomite	$CaMg(CO_3)_2$	1.40	
Muscovite	$KAl_2AlSi_3O_{10}(OH)_2$	1.00	
Galena	Pbs	0.80	
Sphalerite	$(Zn,Fe)S$	0.30	

Table 4.4: "Chalcopyrite 1", "Chalcopyrite 2" and "Pyrite 1" head samples quantitative phase analysis.

Mineral	Ideal Formula	"Chalcopyrite 1" head sample	"Chalcopyrite 2" head sample	"Pyrite 1" head sample
Pyrite	FeS_2	8.00		95.9
Chalcopyrite	$CuFeS_2$	48.6	76.0	
Clinochlore	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$		2.40	
Actinolite	$Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$		1.40	
Pyrrhotite	$Fe_{1-x}S$	35.3		
Clinozoisite	$Ca_2Al_3(SiO_4)_3(OH)$		8.00	
Melanterite	$Fe^{2+}SO_4\ 7H_2O$			1.50
Talc	$Mg_3Si_4O_{10}(OH)_2$			1.60
Quartz	SiO_2	0.70	11.4	1.00
Magnetite	Fe_3O_4	1.30		
Gypsum	$CaSO_4 \cdot 2H_2O$		0.40	
Hydronium Jarosite	$(H_3O^{1+})_2Fe_6{}^{3+}(SO_4)_4(OH)_{12}$		0.40	
Siderite	$Fe^{2+}CO_3$	2.20		

Chapter 5 Results and discussion

5.1 Enargite leaching

Enargite leaching tests included two different samples as previously mentioned; "Enargite 1" and "Enargite 2". The "Enargite 1" sample was used for preliminary tests using glass beakers on a shaker at 70ºC during 24 hours and tests on the agitated reactor at 95º also during 24 hours. These tests served as guidelines for all following tests which were done using sample "Enargite 2", which included the study of the effect of different variables such as temperature, particle size, agitation, pulp density, reagent dosage, etc.

5.1.1 Tests using sample "Enargite 1"

Shaker tests

Shaker tests performed during 24 hours at 70ºC showed a clear tendency of arsenic and antimony to dissolve leaving copper practically untouched. When the concentration of sodium hydroxide and sodium sulphide increases the removal of arsenic and antimony is enhanced, as shown in Table 5.1. On the other hand, copper, zinc and lead do not seem to be affected by the leaching procedure, thus showing the high selectivity of this process towards arsenic and antimony (Nadkarni 1988, Anderson 2008, Curreli 2009, Tongamp 2009). Best results were obtained when using high concentrations of sodium hydroxide and sodium sulphide, which produced a final solid residue containing only 0.25 % of As and 0.01 % Sb.

Table 5.1: Comparison of head sample and leach solid residue from shaker tests

Sample	Content (%)				
	As	Cu	Sb	Zn	Pb
Head Sample	9.30	31.9	0.24	0.30	0.76
NaOH 2.5 M, Na$_2$S 0.0 M	8.75	31.7	0.23	0.28	0.63
NaOH 0.1 M, Na$_2$S 0.5 M	8.26	32.0	0.21	0.30	0.77
NaOH 1.0 M, Na$_2$S 0.5 M	5.33	35.2	0.15	0.33	0.82
NaOH 1.0 M, Na$_2$S 1.0 M	1.33	37.7	0.04	0.35	0.91
NaOH 2.5 M, Na$_2$S 0.5 M	0.72	37.2	0.02	0.34	0.89
NaOH 2.5 M, Na$_2$S 1.0 M	0.25	38.5	0.01	0.36	0.92

Reactor tests

Reactor tests were performed at 95ºC during 24 hours allowing, unlike during shaker tests, to draw samples during the test itself. Samples were taken at 1, 2, 4, 8 and 24 hours, following the same trend of the shaker tests, which increased removal of arsenic and antimony as concentration of sodium hydroxide and sodium sulphide were incremented. Again all other metals, such as copper, zinc and lead remained un-leached. Results suggest that in the cases where complete removal took place, it is reached before 5 hours of leaching. This information was taken into account in the following tests which were done with the sample "Enargite 2"

5.1.2 Tests using sample "Enargite 2"

5.1.2.1 Effect of temperature

Note, all NaOH concentrations reported consider only the amount added as a solid, and the NaOH produced by the hydrolization of Na$_2$S is only reported when analysing the effect of stoichiometry in high pulp density tests.

Leaching tests were carried out at 50, 65, 80 and 95ºC while keeping all other variables constant which included 10 grams of enargite sample in 200 ml of leach solution containing 2.5 M NaOH and 1.0 M Na$_2$S, agitated at 500 RPM during 2 hours. Results show a clear improvement in the kinetics of arsenic and antimony removal as temperature is increased. This strong temperature dependence suggests that the controlling mechanism could be the chemical reaction taking place on the surface of the particles. In the case of copper, removal remains below 0.5 % at 50ºC and decreases as temperature is increased up to 95ºC. Again, other metals such as zinc, lead, iron and nickel show practically no solubilisation and in many cases are below detections limits in solution. Figures 5.1 to 5.3 show the results obtained.
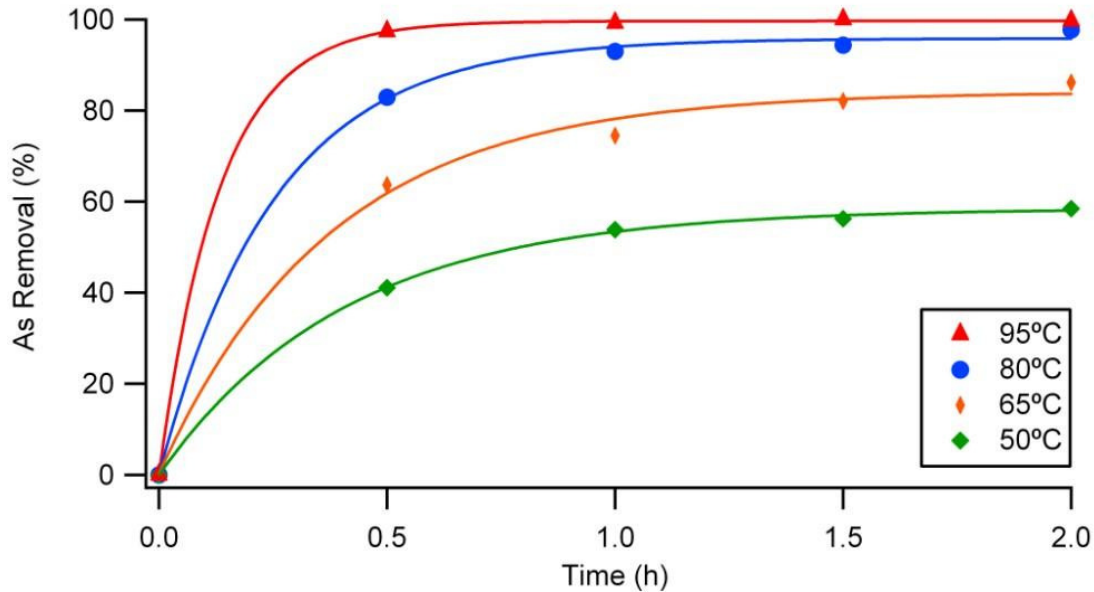
Figure 5.1: Effect of temperature on As removal using 10 g of enargite sample with a P$_{80}$ of 30 μm in 200 ml of solution 2.5 M NaOH and 1.0 M Na$_2$S at 500 RPM stirring velocity.
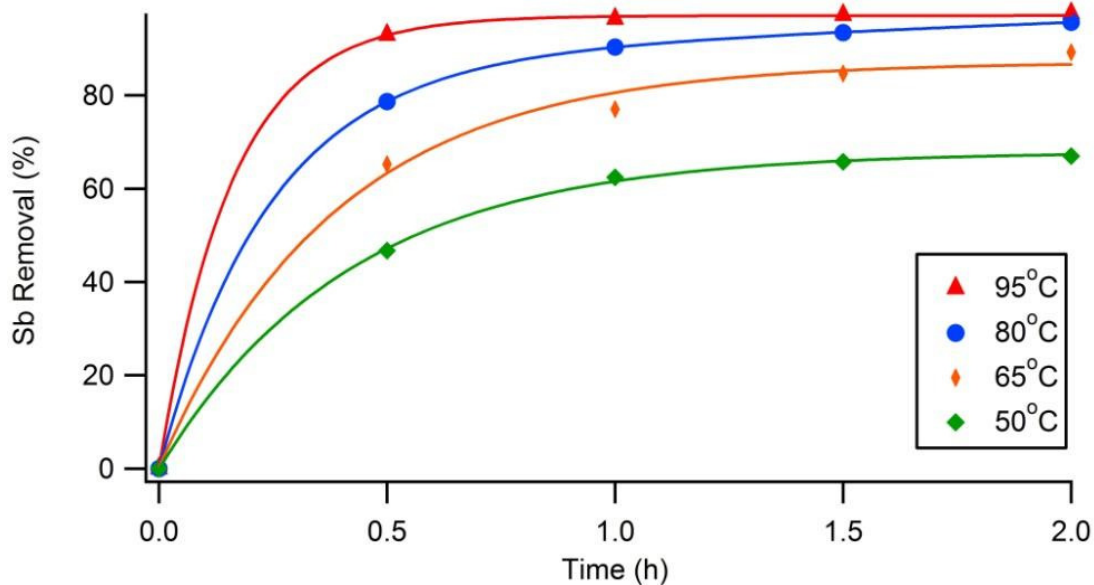
Figure 5.2: Effect of temperature on Sb removal using 10 g of enargite sample with a P_{80} of 30 μm in 200 ml of solution 2.5 M NaOH and 1.0 M Na_2S at 500 RPM stirring velocity.
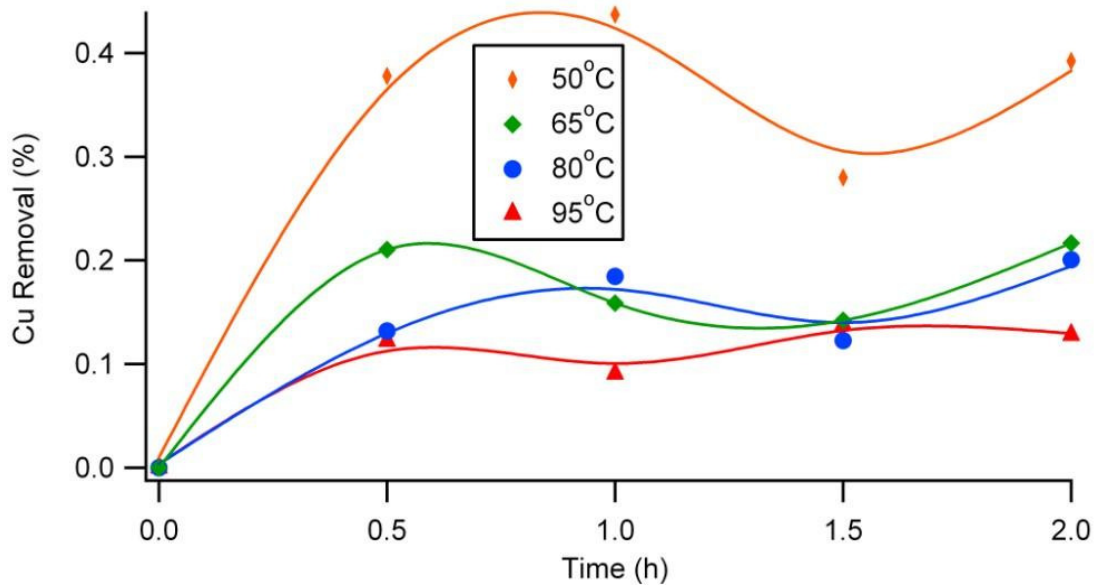
Figure 5.3: Effect of temperature on Cu removal using 10 g of enargite sample with a P_{80} of 30 μm in 200 ml of solution 2.5 M NaOH and 1.0 M Na_2S at 500 RPM stirring velocity.

5.1.2.2 Effect of sodium hydroxide and sodium sulphide concentration

The alkaline leaching of enargite using sodium sulphide depends, amongst other factors, on the concentration of sodium hydroxide and sodium sulphide used. Some authors (Nadknarni 1988, Curreli 2009) suggest that sodium hydroxide works as a means of stabilizing sulphide ions in solution, so that they can solubilise the arsenic. However there is evidence that sodium sulphide will dissociate as sodium hydrosulphide at pH below 17 or perhaps higher than 17 (Giggenbach 1971, Licht 1988), meaning arsenic will react with hydrosulphide and hydroxide instead of sulphide ions, as suggested by Tongamp *et al* (Tongamp 2009, 2010). In order to analyze these possibilities, several tests have been performed at a temperature of 95ºC, in 200 ml of alkaline sulphide solution, with 10 g of enargite sample agitated at 500 RPM using a magnetic stirrer. The concentrations chosen are shown in Table 5.2.

Table 5.2: Sodium hydroxide and sodium sulphide concentrations tested

Experiment	NaOH (M)	Na_2S (M)	Theoretical pH
1	2.5	1.0	14.54
2	2.5	0.5	14.48
3	1.0	1.0	14.30
4	0.1	1.0	14.04
5	1.0	0.5	14.18

The effect of sodium hydroxide and sodium sulphide concentration on arsenic and antimony can be seen on Figures 5.4 and 5.5.
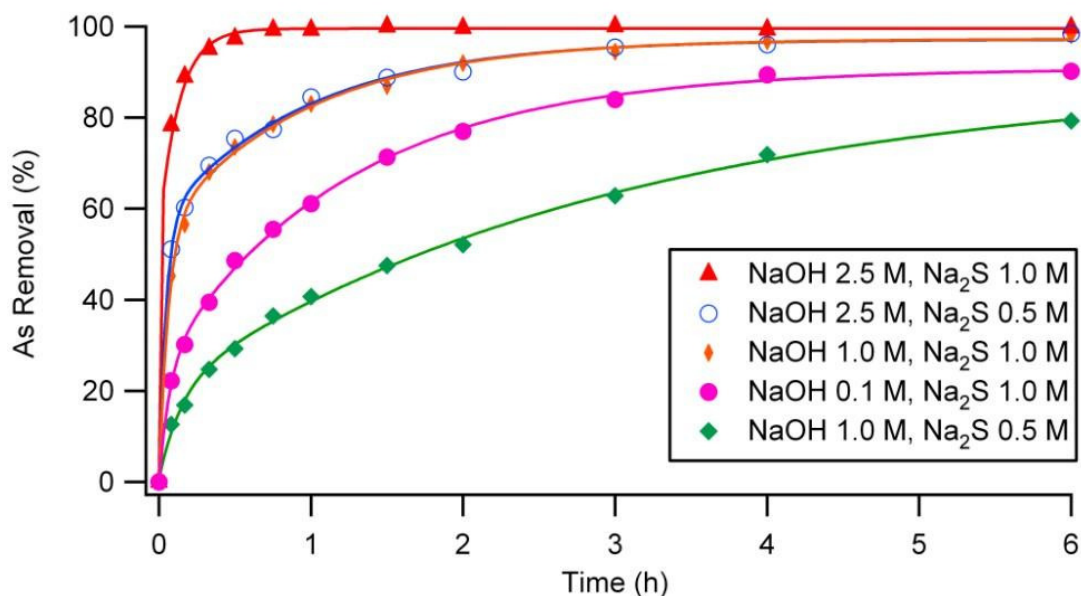
Figure 5.4: Effect of NaOH and Na₂S on As extraction at 95ºC using 10 g of enargite sample with a P₈₀ of 30 μm in 200 ml of solution and 500 RPM.
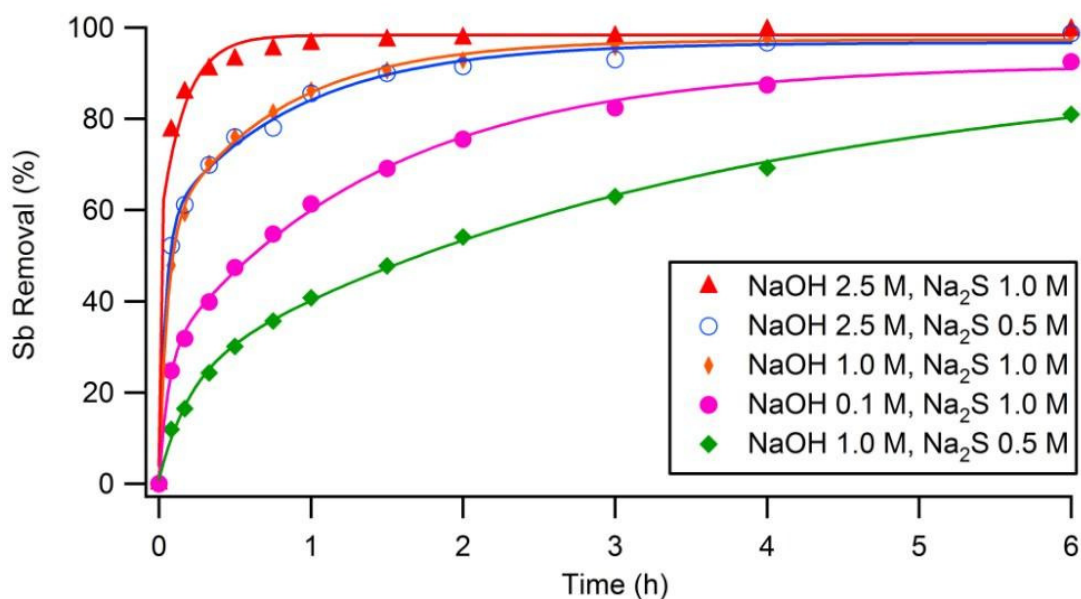
Figure 5.5: Effect of NaOH and Na₂S on Sb extraction at 95ºC using 10 g of enargite sample with a P₈₀ of 30 μm in 200 ml of solution and 500 RPM.
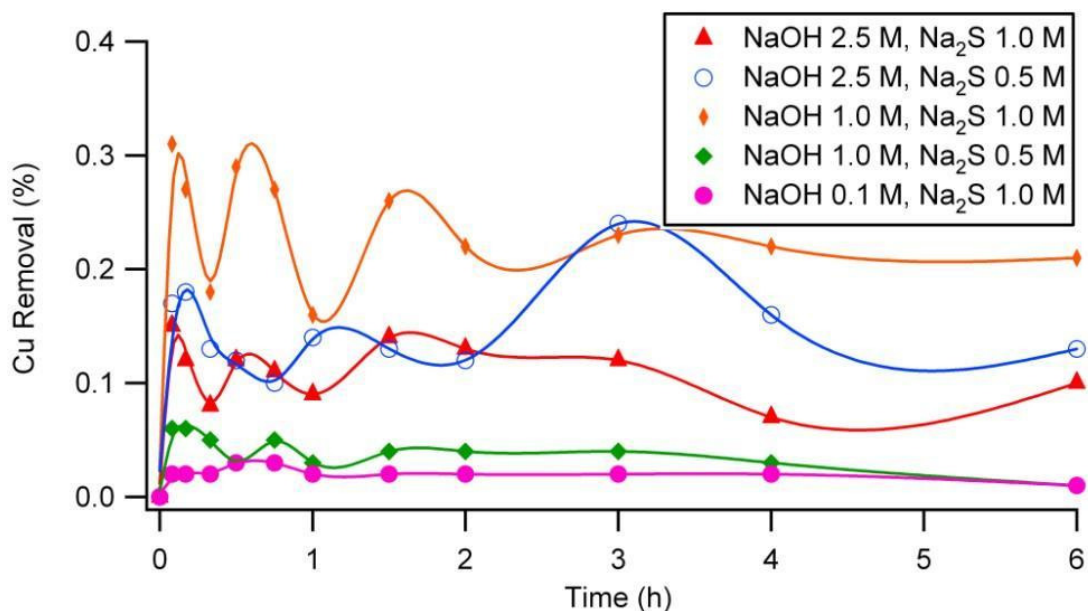
Figure 5.6: Effect of NaOH and Na₂S on Cu extraction at 95ºC using 10 g of enargite sample with a P₈₀ of 30 μm in 200 ml of solution and 500 RPM.

Best results are obtained when both reagents are added in high amounts (2.5 M NaOH and 1.0 M Na₂S). Almost complete removal of arsenic and antimony is obtained within 1 hour.

When modifying the concentration of either reagent, it can be observed that if sodium hydroxide concentration is lowered to 1.0 M, and sodium sulphide concentration is kept at 1.0 M, kinetics decrease; however, after 3 hours arsenic and antimony removal reaches approximately 95 %. On the other hand, if sodium sulphide concentration is lowered to 0.5 M, and sodium hydroxide is increased to 2.5 M, the behaviour of arsenic and antimony is very similar to the 1 M reagent concentration test. This behaviour could suggest that both reagents are acting directly in the dissolution of arsenic and antimony instead of sodium hydroxide being only used to stabilize the sulphide ions.

In fact, all tests shown here, have been run at a sodium hydroxide concentration that would provide a pH higher than the buffer point between hydrosulphide and sulphide ions proposed by some authors (pH ~ 12) (Anderson 2008), therefore, one could expect to see a lesser effect in the dissolution kinetics when lowering the sodium hydroxide

concentration, such as the case of the test run at 0.1 M sodium hydroxide and 1 M sodium sulphide.

All these tests were performed with a large excess of reagent. Table 5.3 shows the reagent to arsenic plus antinomy ratios used and the content of arsenic and antimony in the solid residue. The results support the idea that both hydroxide and sulphide are acting in the leaching process and that there is no passivation of the enargite particles. The reaction takes place quickly until reaching approximately 100 % when using high reagent doses, or happens more slowly when using lower reagent doses, but it does not seem to stop occurring.

Table 5.3 Sodium hydroxide plus sodium sulphide over arsenic plus antimony molar ratios according to Equation 3.4.6 and content of As and Sb in the leach residue after leaching for 6 hours.

NaOH/(As+Sb) Stoichiometric molar ratio	Na$_2$S/(As+Sb) Stoichiometric molar ratio	[NaOH] (M)	[Na$_2$S] (M)	NaOH/(As+Sb) actual molar ratio	Na$_2$S/(As+Sb) actual molar ratio	As in solid residue (%)	Sb in solid residue (%)
		2.5	1.0	31.3	12.5	0.067	0.004
		2.5	0.5	31.3	6.25	0.257	0.008
1.5	1.5	1.0	1.0	12.5	12.5	0.324	0.009
		0.1	1.0	1.25	12.5	1.232	0.052
		1.0	0.5	12.5	6.25	3.852	0.145

Table 5.4: Comparison of solid residue with head sample after leaching during six hours at 95° and different concentrations of NaOH and Na$_2$S

Sample	Cu (%)	Fe (%)	Zn (%)	Ag (%)
Head	40	12	0.316	0.0193
2.5 M NaOH – 1.0 M Na$_2$S	48.48	12.70	0.362	0.0243
1.0 M NaOH - 1.0 M Na$_2$S	48.49	15.66	0.346	0.0239
0.1 M NaOH - 1.0 M Na$_2$S	42.39	12.45	0.330	0.0241
2.5 M NaOH - 0.5 M Na$_2$S	49.17	15.87	0.384	0.0246
1.0 M NaOH - 0.5 M Na$_2$S	45.65	14.64	0.342	0.0229

5.1.2.3 Effect of stoichiometry on high pulp density tests

The effect of different concentrations exceeding the stoichiometric amount of sodium hydroxide and sodium sulphide according to Equation 3.4.6 on high pulp density tests (200 grams of sample in 200 ml of leach solution) can give information not only about the kinetics and efficiency of the reagents added, but also about potential filtration issues due to high viscosity of the pulp after leaching or the small particle size of the leach residue (Ackerman 1993).

Tests were conducted adding 200 grams of "Enargite 2" sample in 200 ml of leach solution containing 100 %, 150 % and 200 % of the required amount of sodium sulphide and 200 %, 300 % and 400 % of sodium hydroxide respectively. Only tests using 100 % of the stoichiometric amount of sodium sulphide and 200 % of sodium hydroxide were easily filtered, whereas the other two had difficulties probably due to excessive particle size reduction and high viscosity of the slurry. During filtration of these two last samples some small particles made it through, however the worst issue was the time of filtration that could reach up to one hour, especially during washing of the cake.

The results seen in Figures 5.7 to 5.9 show that arsenic extraction reached a value of approximately 75 % after 30 minutes of leaching, which increased to 85 when using 150 % of the required sodium sulphide and to 95 % extraction with 200 % of the required sulphide. A similar situation is seen in the case of antimony; however the increase in extraction is not as pronounced as in arsenic removal when increasing reagent concentration. Again, copper removal is small, not above 0.2 %. The same behaviour is seen for other metals like iron, zinc and silver, which are practically not solubilised at all.
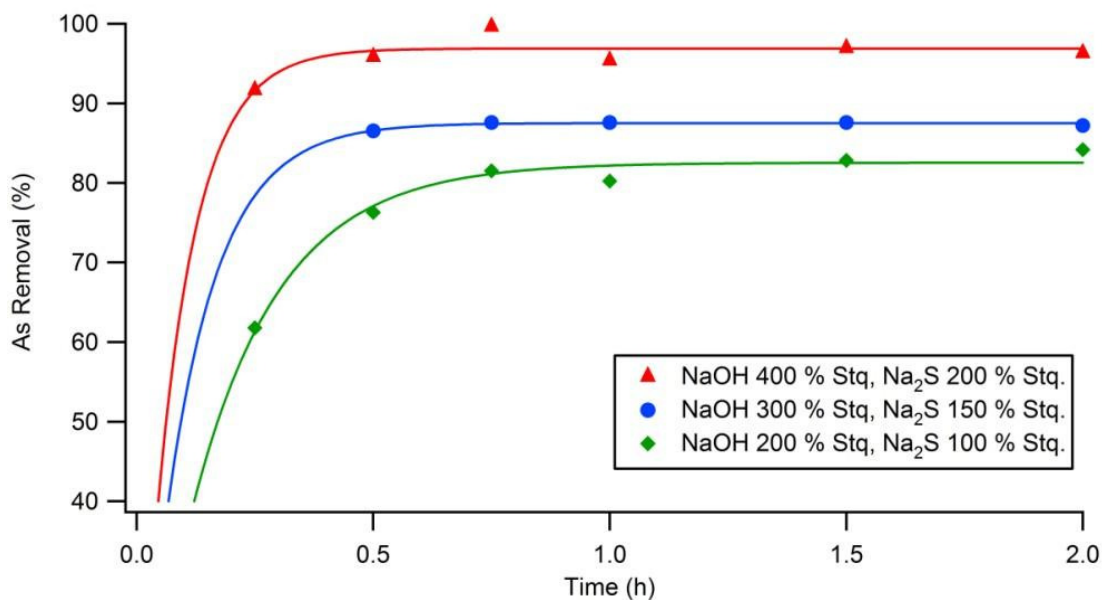
Figure 5.7: Effect of stoichiometry on As removal at 95ºC using 200 g of enargite sample with a P_{80} of 30 µm in 200 ml of solution and 500 RPM during 2 hours.
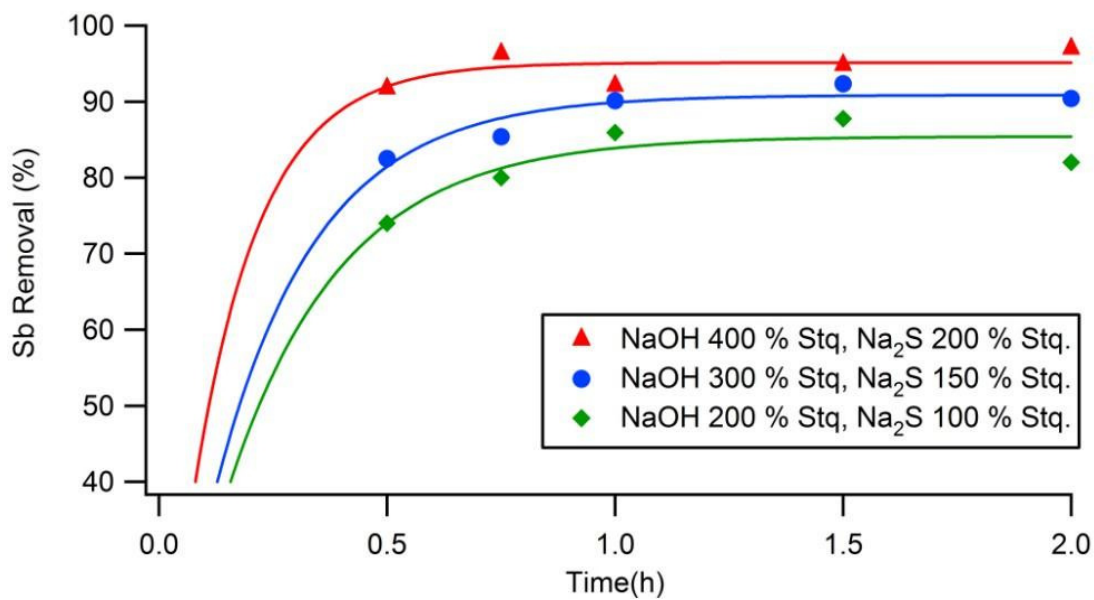
Figure 5.8: Effect of stoichiometry on Sb removal at 95ºC using 200 g of enargite sample with a P_{80} of 30 µm in 200 ml of solution and 500 RPM during 2 hours.
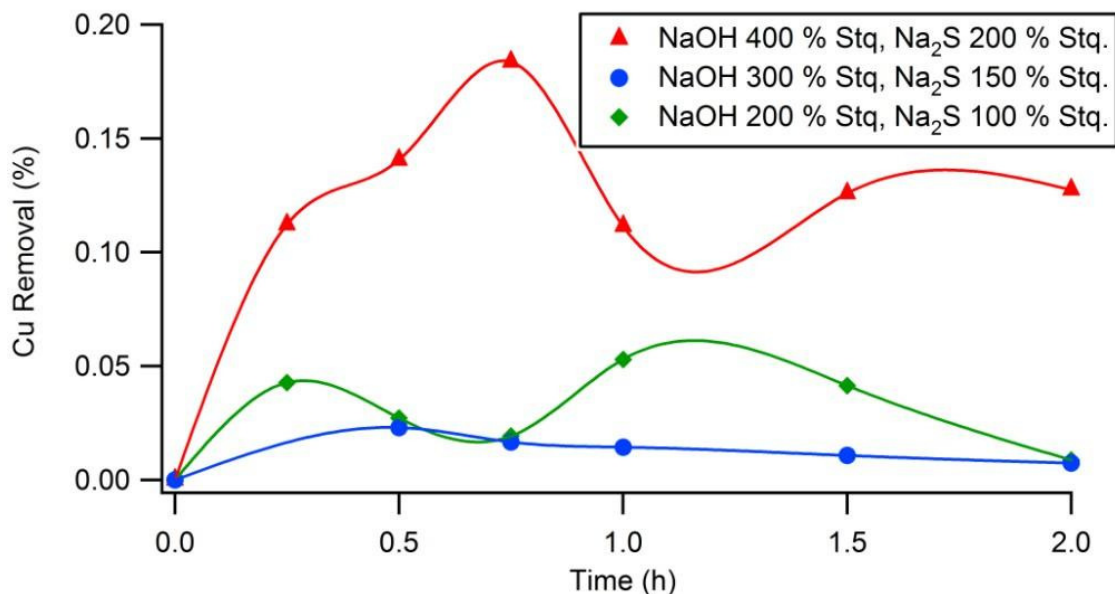
Figure 5.9: Effect of stoichiometry on Cu removal at 95ºC using 200 g of enargite sample with a P_{80} of 30 μm in 200 ml of solution and 500 RPM during 2 hours.

Leaching tests at 100 % of stoichiometric sodium sulphide and 200 % of sodium hydroxide did not produce filtration issues, however a solid residue containing over 1 % of arsenic was produced. In order to further reduce the arsenic content the solid residue was leached twice more using the same amount of sulphide and hydroxide as in the first test. These amounts gave sulphide to arsenic and antimony molar ratios of approximately 10 and 60 times the stoichiometric amounts needed and hydroxide to arsenic and antimony molar rations of 20 and 120 times the stoichiometric amount necessary for the second and third stage respectively. Even though these amounts are large, the solutions could be recirculated and reused or concentrations reduced in order to optimise the process. Also, according to Figure 5.10 and Table 5.11, it seems that the process could be run in two stages of only 30 minutes to one hour each and reach an arsenic value of less than 0.5 % in the residue.

Table 5.5: As, Cu and Sb content on the solid residue after leaching by stages

Stage	As (%)	Cu (%)	Sb (%)
1st	2.620	38.89	0.053
2nd	0.237	36.42	0.012
3rd	0.026	40.24	0.004
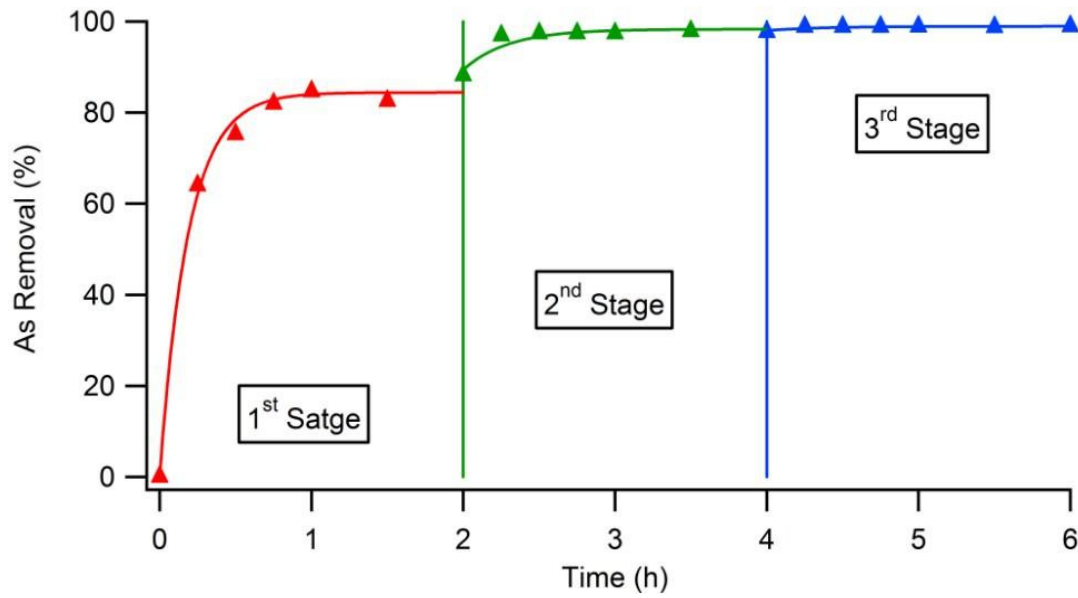
Figure 5.10: Three stage leaching of enargite using conditions from Figure 5.7. Effect on arsenic removal.
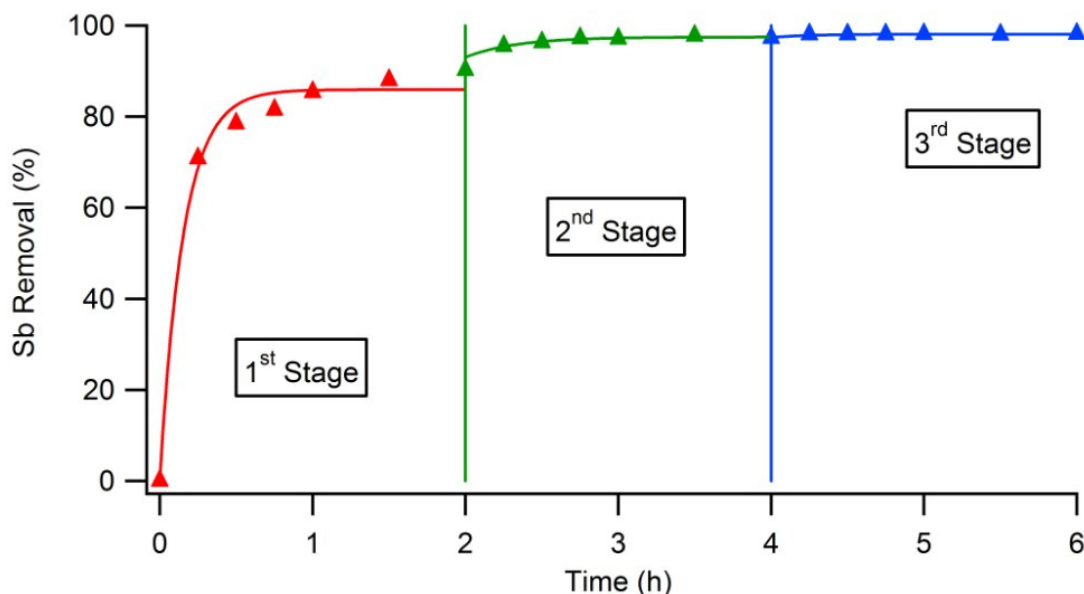
Figure 5.11: Three stage leaching of enargite using conditions from Figure 5.7. Effect on antimony removal.

5.1.2.4 Effect of particle size

In leaching processes particle size is crucial since it is directly related to the liberation/exposure of the elements/compounds to be leached. The finer the size the larger surface area available for the reactions to take place and the faster the kinetics should be. However there must be a balance between cost of the reduction size steps and the particle size requirements of previous and following steps.

In this particular case, kinetics were improved as particle size was decreased from a P_{80} of 90 to 60 to 30 microns. The improvement of As and Sb removal is evident as particle size is decreased as it can be seen in Figures 5.12 and 5.13, which suggests a diffusion controlled process, and Cu shows a slight increase as well but never over 0.2 % of removal as seen in Figure 5.14.
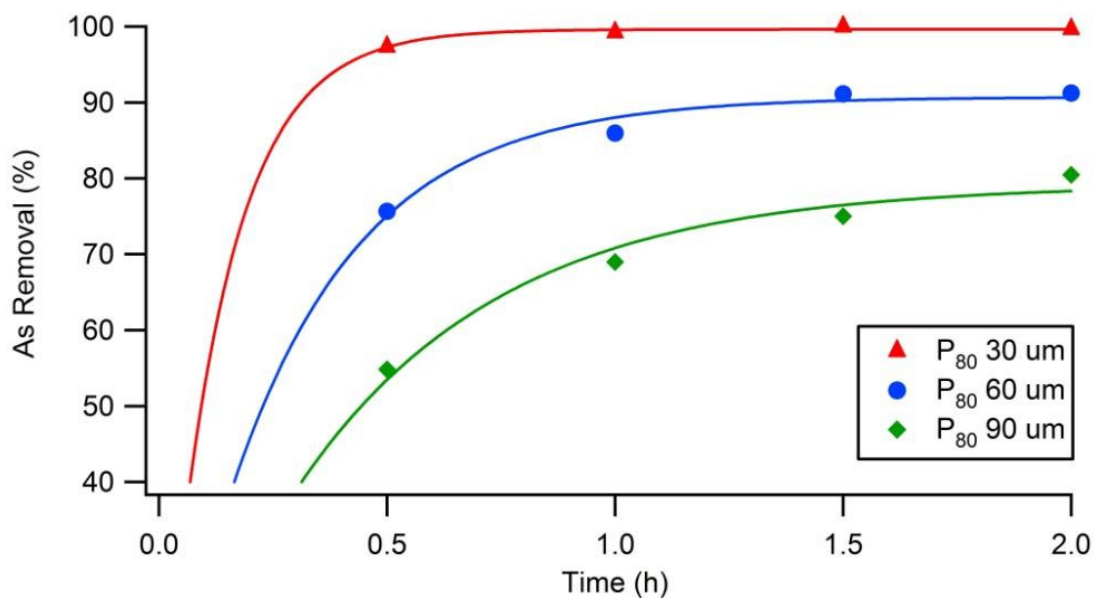
Figure 5.12: Effect of particle size on As removal at 95ºC using 10 g of enargite sample in 200 ml of solution, 2.5 M NaOH and 1.0 M Na₂S and 500 RPM during 2 hours.
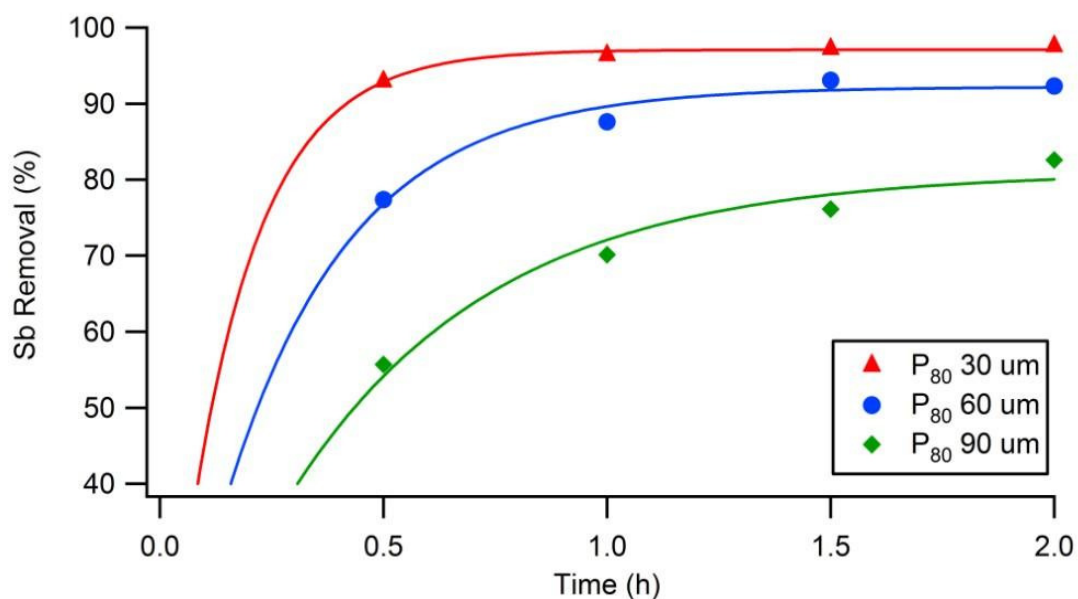
Figure 5.13: Effect of particle size on Sb removal at 95ºC using 10 g of enargite sample in 200 ml of solution, 2.5 M NaOH and 1.0 M Na₂S and 500 RPM during 2 hours.
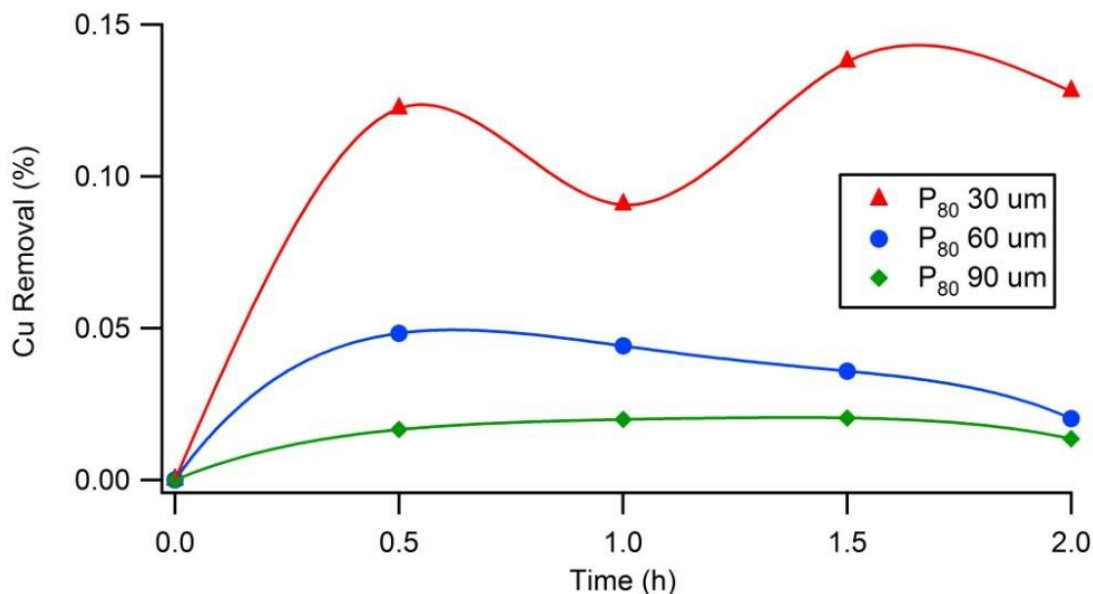
Figure 5.14: Effect of particle size on Cu removal at 95ºC using 10 g of enargite sample in 200 ml of solution, 2.5 M NaOH and 1.0 M Na₂S and 500 RPM during 2 hours.

5.1.2.5 Effect of agitation

In leaching processes where agitation speed has a significant effect the controlling mechanism could be mass transfer in the stagnant film. This is relevant to the process because ideally one would want to run the procedure at an agitation speed which is above the mass transfer limitation.

Figures 5.15 and5.16 show results obtained when leaching "Enargite 2" samples at agitation speeds of 60, 120, 240, 500 and 750 RPM. After one hour of leaching it can be seen that removal of arsenic and antimony is not considerably affected by changing stirring velocity, which suggests the controlling mechanism is not mass transfer limited.

Results show that in the case of arsenic there is a maximum difference between highest and lowest extraction in some points of approximately 10 %, but overall the effect is small and in the case of antimony the effect of agitation is even smaller.

These facts together with the strong effect of temperature and particle size on the performance of the alkaline sulphide leach, suggest that the controlling mechanism could be chemical or diffusion in a solid layer.
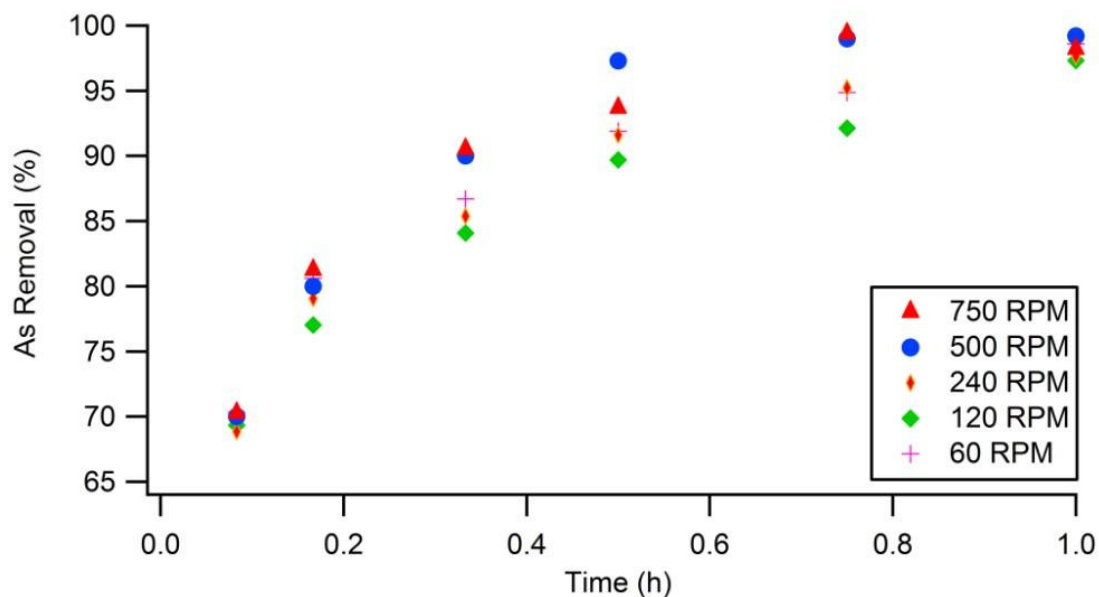
Figure 5.15: Effect of agitation on As removal at 95ºC using 10 g of enargite sample in 200 ml of solution, 2.5 M NaOH and 1.0 M Na₂S and a P80 of 30 μm during 2 hours.
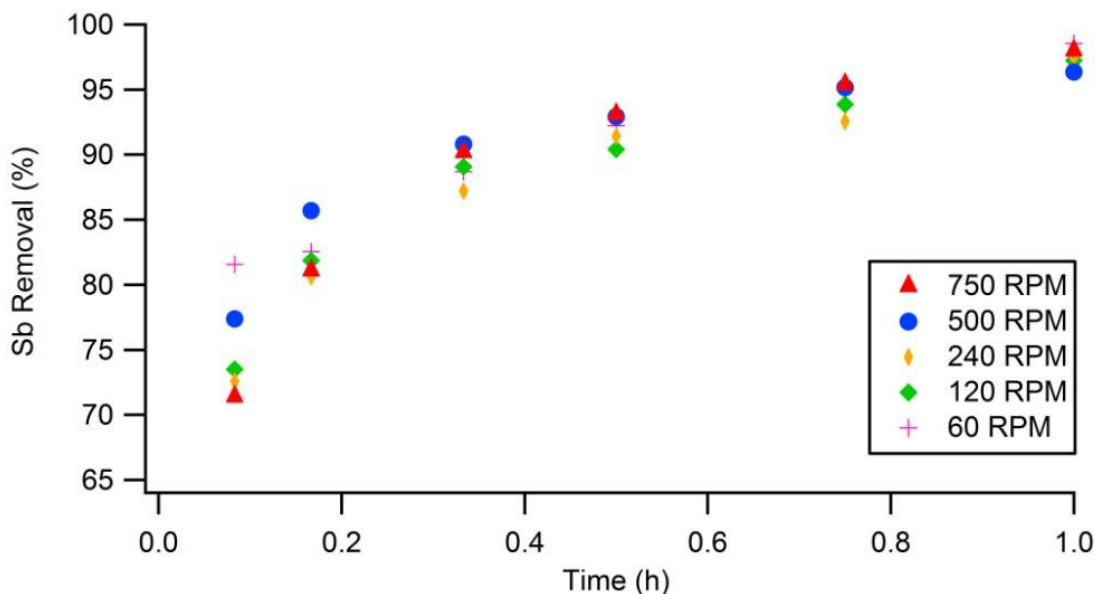
Figure 5.16: Effect of agitation on As removal at 95ºC using 10 g of enargite sample in 200 ml of solution, 2.5 M NaOH and 1.0 M Na$_2$S and a P80 of 30 μm during 2 hours.

5.2 Solid residue analysis

The solid residue produced after the leach is rich in copper and must be suitable for further treatment. Therefore, the residues generated must be filterable and the arsenic content must be lowered to below 0.5 % by weight in order to be accepted by smelters (Filippou 2007).

Scanning Electron Microscopy (SEM) and EDX analyses can help elucidate what the leaching mechanism might be and provide information regarding morphology of the new solid phases formed. Qualitative and quantitative (Rietveld method) X-Ray Diffraction was also used to try to characterize the solid residues and identify any new phases which may form.

SEM micrographs seen in Figures 5.17 to 5.19 show a non polished sample of non leached "Enargite 1" and "Enargite 2", with a map showing arsenic distribution, some silica and a few small particles of pyrite.
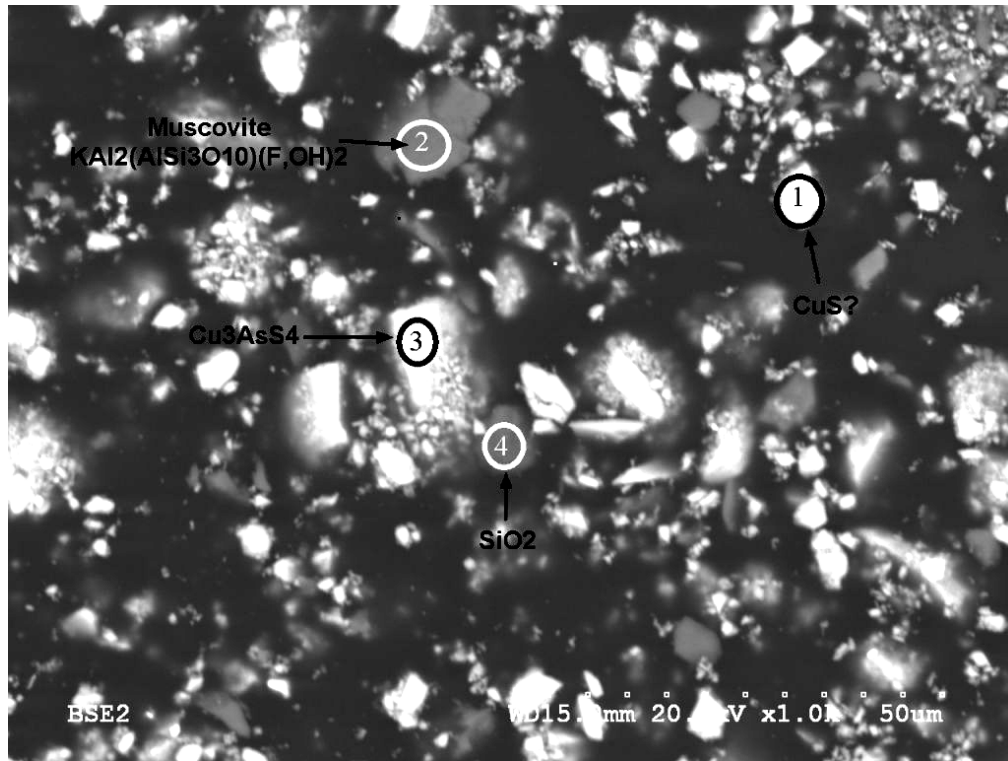
Figure 5.17: "Enargite 1" head sample
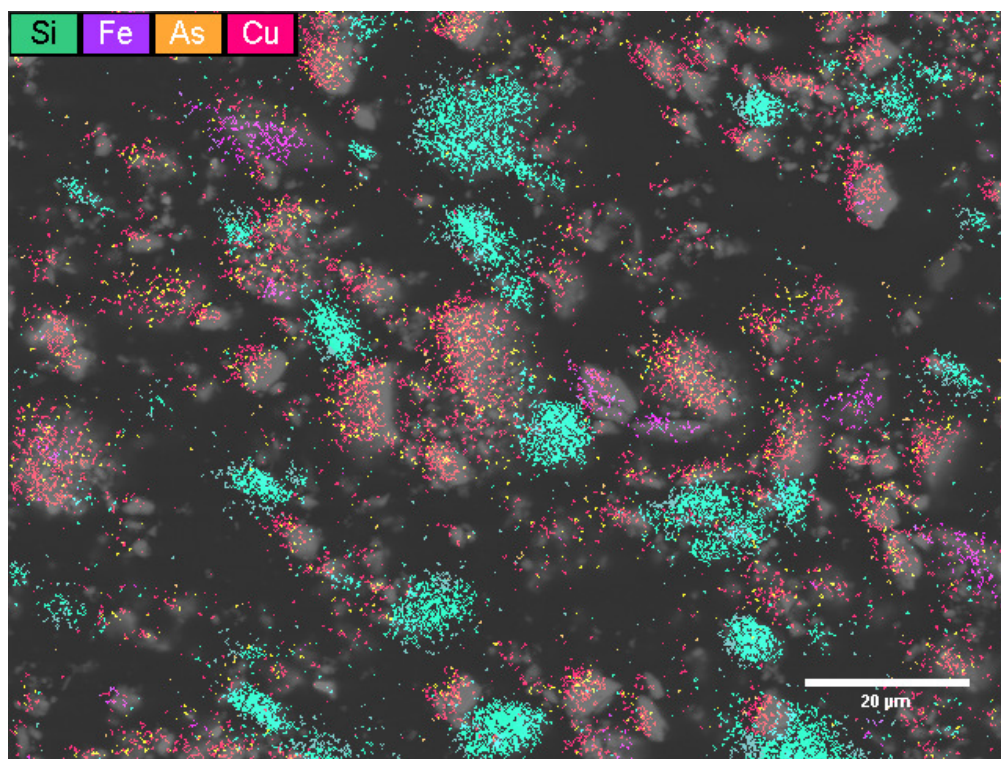
Figure 5.18: "Enargite 1" head sample.
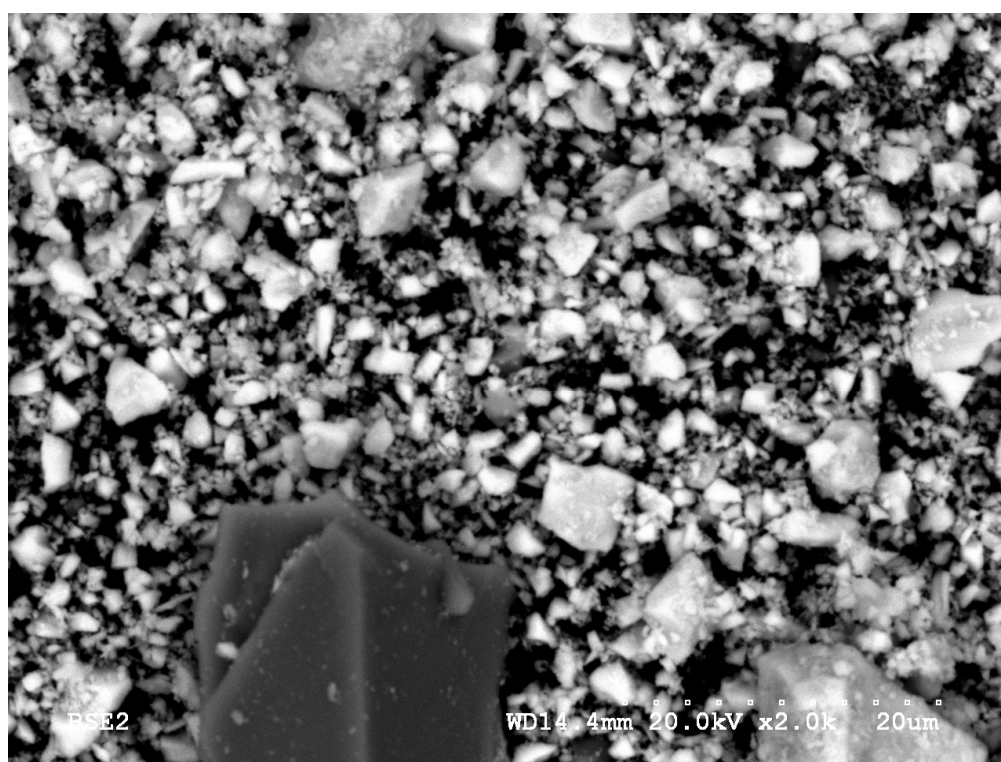
Figure 5.19: "Enargite 2" head sample

After being leached, in both samples, silica, pyrite, lead sulphides, zinc sulphides and copper sulphides (except enargite) seemed unaltered. Leached samples show very fine grains of some type of copper-sulphur phase when analysed with EDX. This new phase formed has been studied in the past and regarded as chalcocite or some other type of copper sulphide such as $Cu_{3.9}S_{2.8}$ or $Cu_{1.5}S$ as well as jarosites (Achimovičová 1999, Curreli 2009). Figures 5.20 to 5.32 show leached samples of both enargite samples.
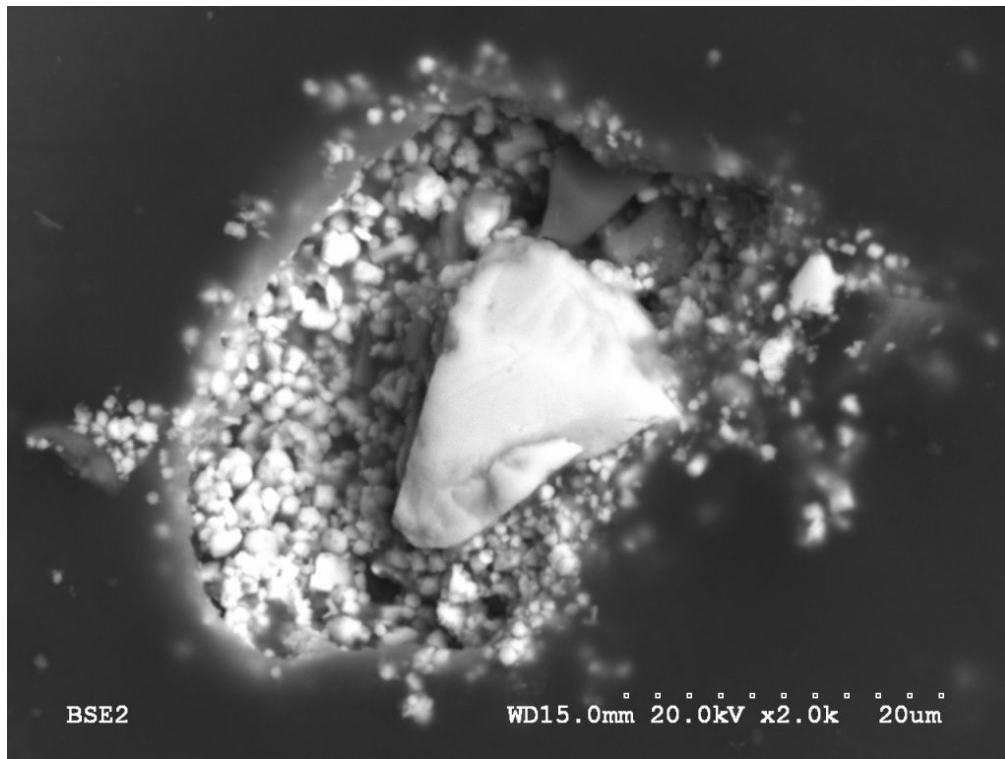
Figure 5.20: Micrograph of leach residue of "Enargite 1" sample showing an unleached zinc sulphide particle and a new copper-sulphur phase formed.

Curreli *et al* (Curreli 2009) reports there is an unreacted core of enargite, surrounded by the new copper phase formed, which suggests the leaching mechanism would follow the shrinking core model. However, in the case of samples "Enargite 1" and "Enargite 2", it can be seen that enargite seems to dissolve and recrystallize as discrete particles of a copper sulphide phase which is very low in arsenic and any sign of enargite seems absent. Thus it is unlikely that these particles grow around an unreacted core. This can be seen more clearly in Figures 5.24 to 5.26.
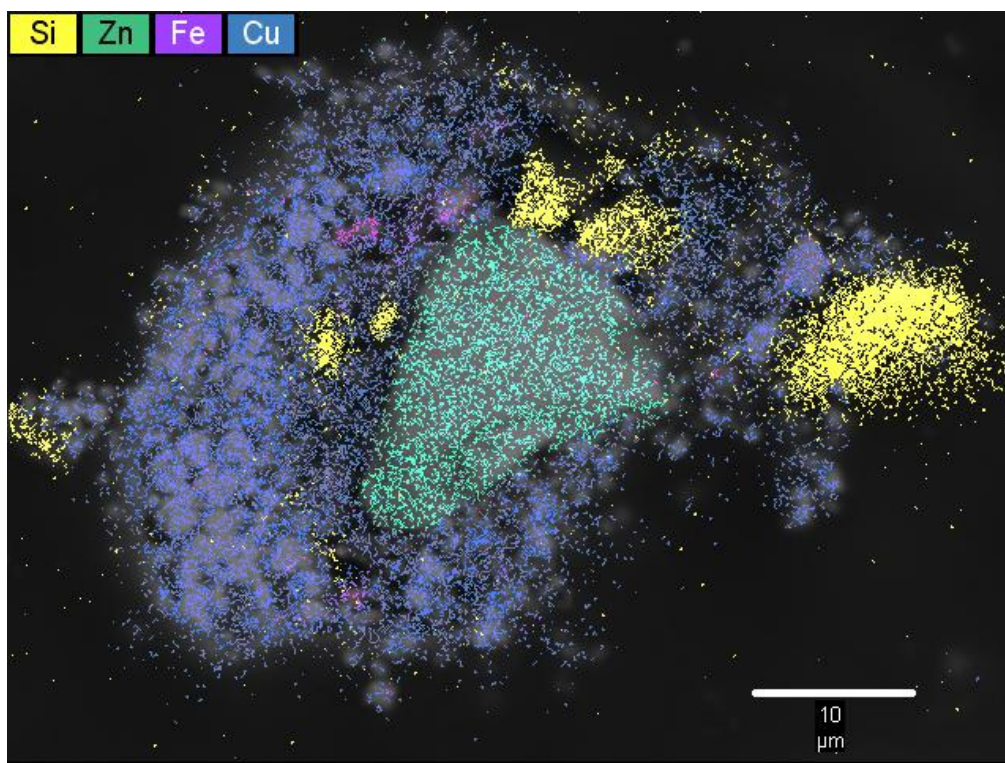
Figure 5.21 Map of Figure 5.16 showing Si, Zn, Fe and Cu distribution.

Figure 5.24 shows a partially leached residue of sample "Enargite 2" and Figures 5.25 and 5.26 show the distribution of arsenic and copper respectively, where arsenic bearing particles do not show any kind of layer surrounding them and it can be seen that copper rich particles without arsenic are distributed in a way that seems random. Again in these pictures, it can be seen that Si bearing particles (most likely silica) and Fe bearing particles (most likely pyrite) do not seem to be affected by the leaching procedure.
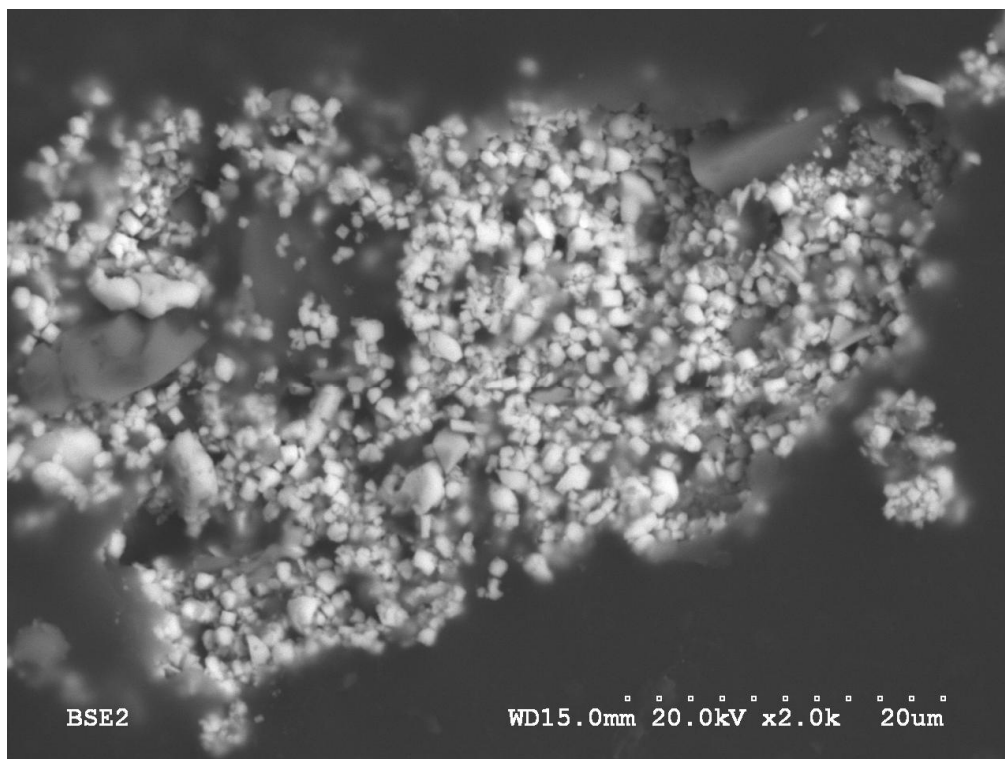
Figure 5.22: New crystals of Cu-S formed after leaching sample "Enargite 1"
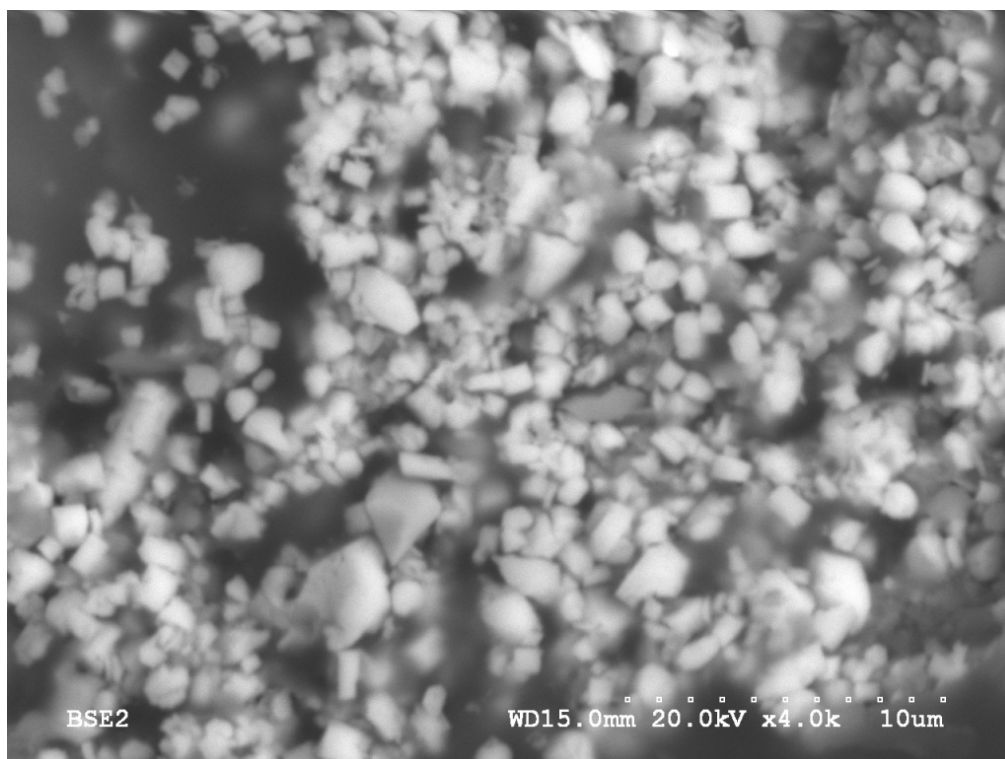
Figure 5.23: Magnification of Figure 5.19
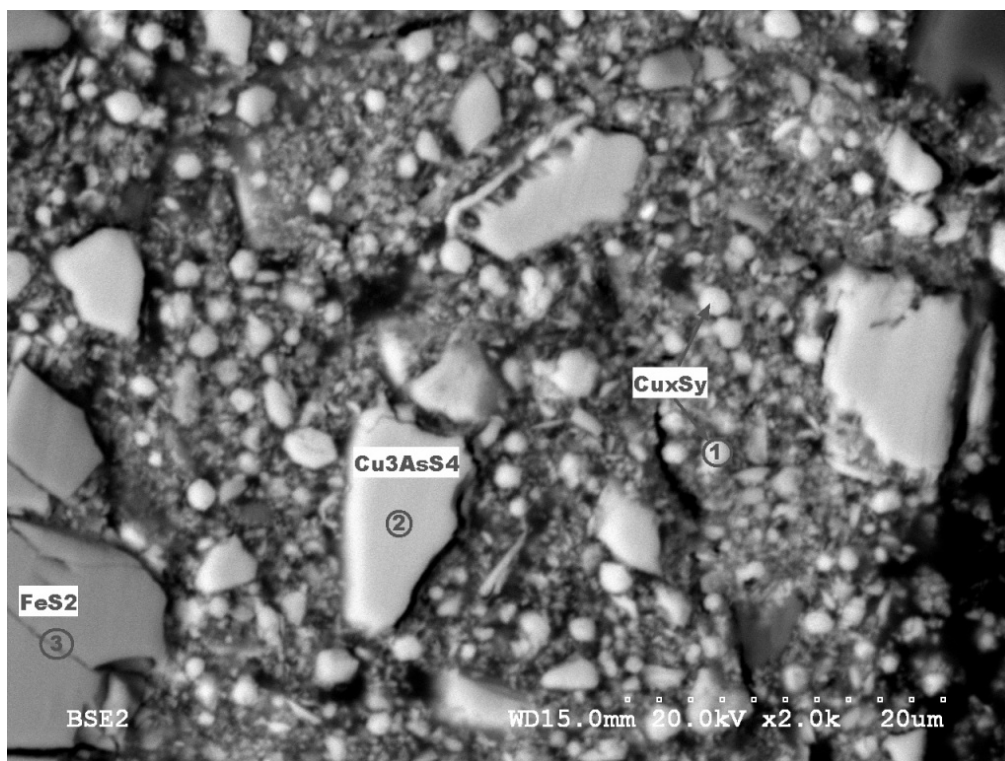
Figure 5.24: Partially leached "Enargite 2" sample
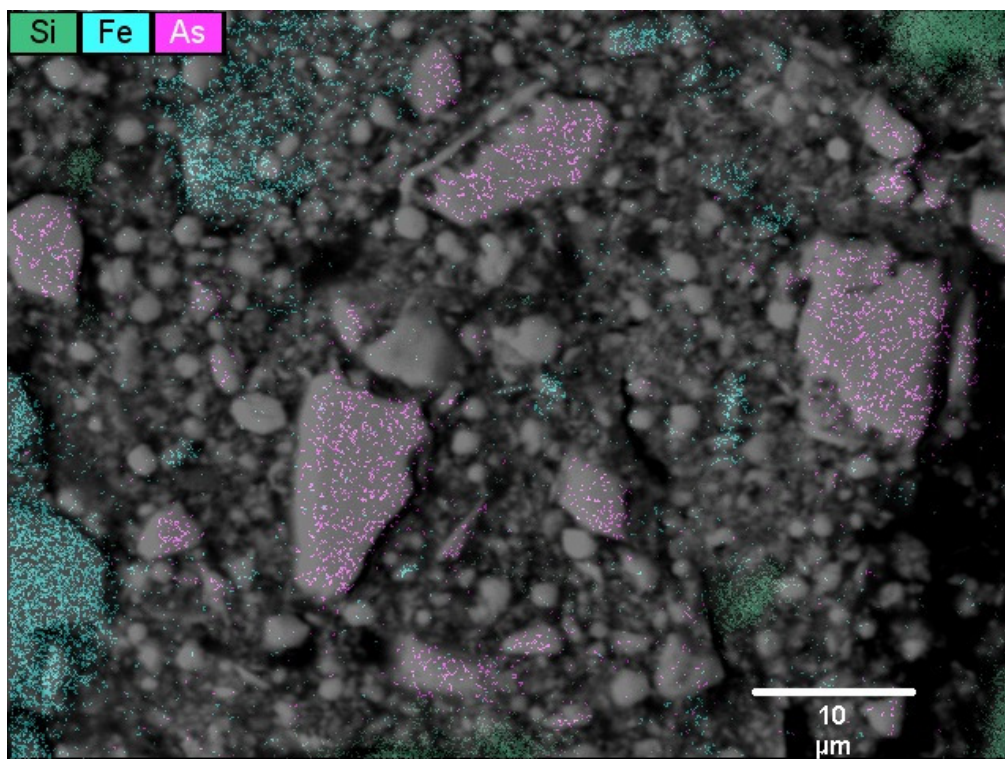
Figure 5.25: Figure 5.19 distribution of As, Fe and Si.
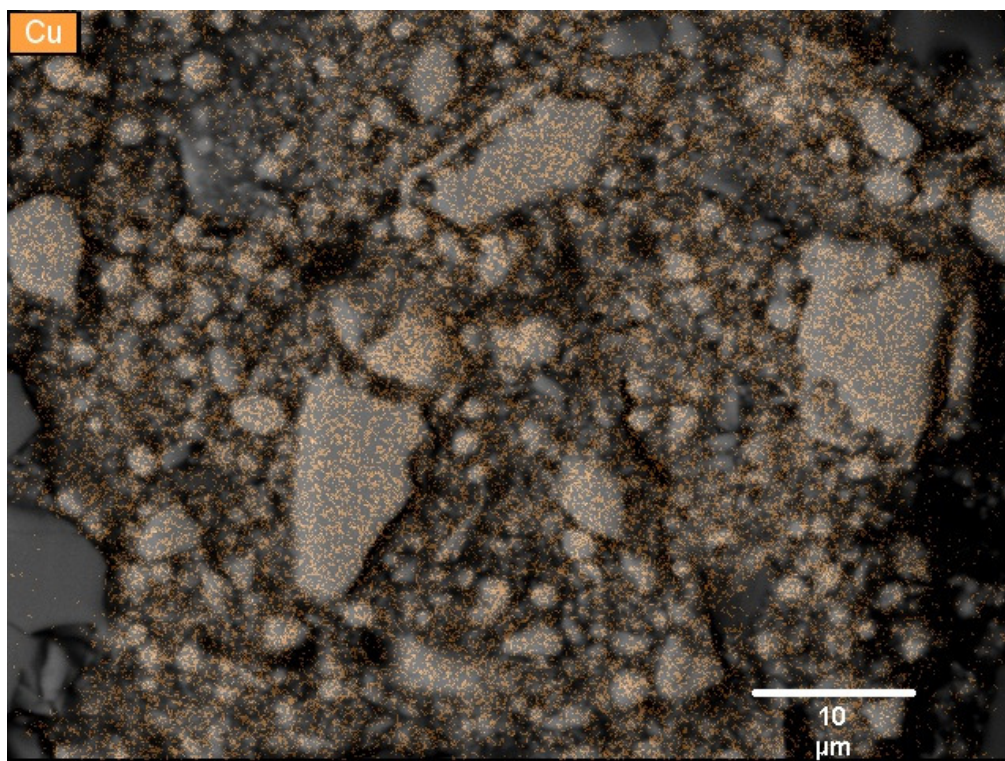
Figure 5.26: Figure 5.19 distribution of Cu
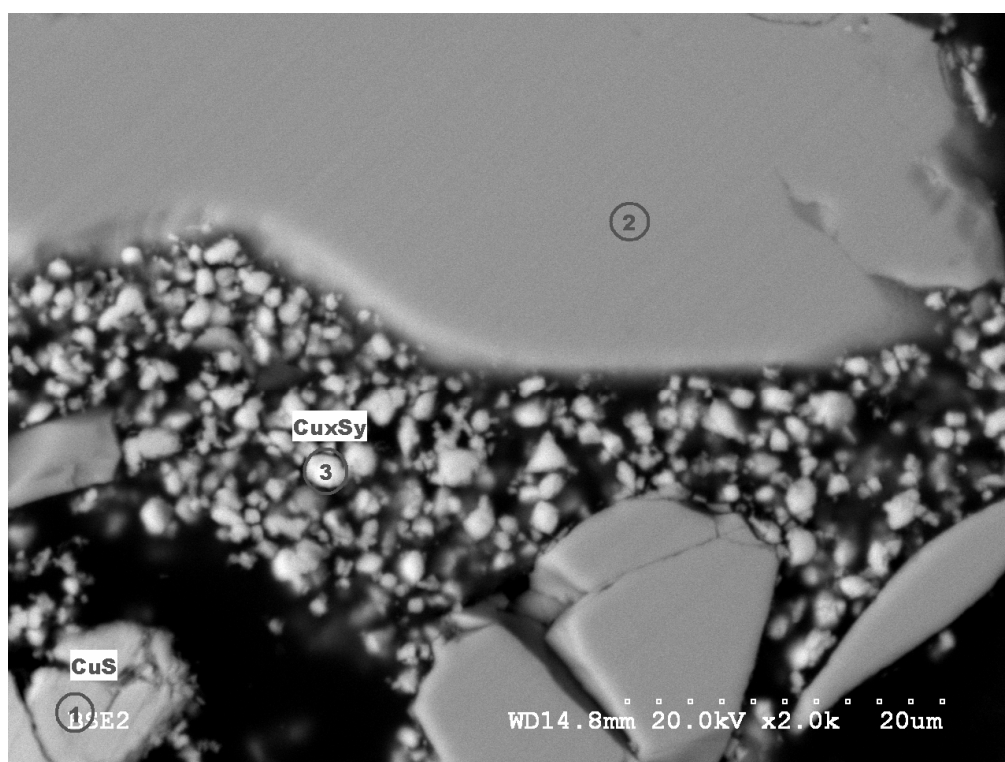
Figure 5.27: "Enargite 2" leached residue showing a large pyrite particle and the new phase formed

However, Figures 5.20 to 5.28 show micrographs taken from leach residue powders mounted on epoxy which are then ground and polished before being observed under the microscope. This procedure may have modified the morphology of the leach residues. In order to try to confirm the theory that the new copper phase forms as discrete particles rather than a product surrounding unreacted enargite cores, solid residue samples were put under the microscope as powders. Figures 5.29 to 5.32 show these samples where the same type of particles seen in the polished samples appear.
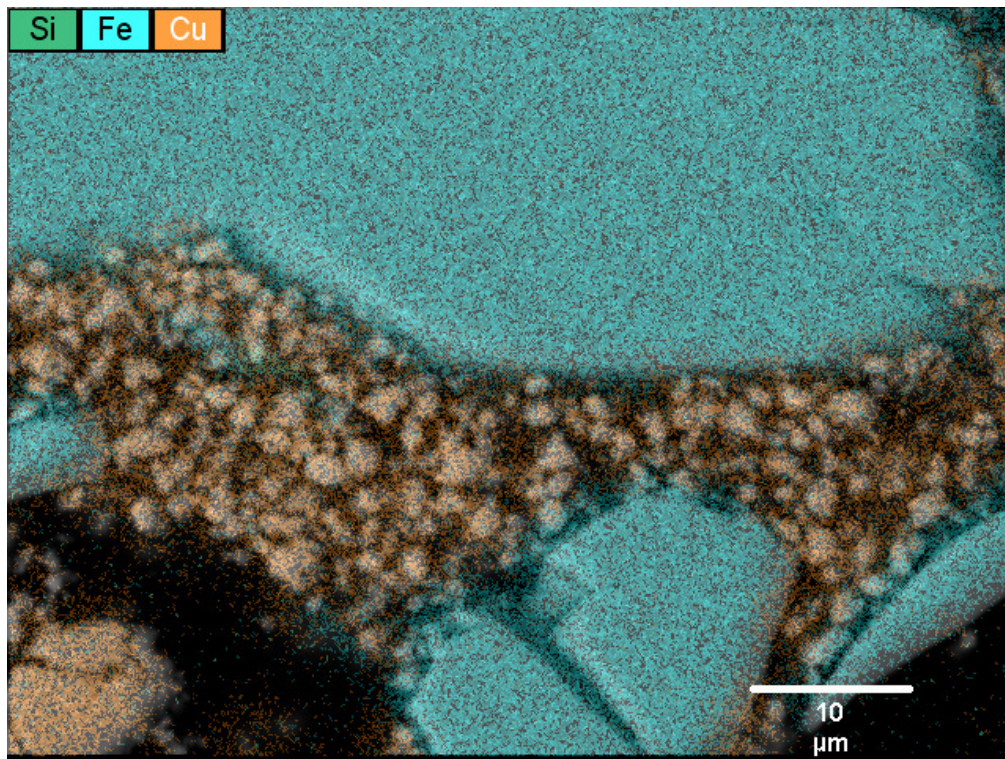
Figure 5.28: "Enargite 2" leached residue showing a large pyrite particle and the new phase formed

Even though the new phase formed appears to contain mainly copper and sulphur, it has proven difficult to determine its exact nature. X-Ray Diffraction analyses using the Rietveld method were performed to obtain a detailed phase composition of the leach residues. "Enargite 1" samples showed the presence of digenite (Cu_9S_5) after being leached for 24 hours. In the case of "Enargite 2" samples, determining the new phase was more difficult, probably due to the fact that leaching tests lasted 6 hours or less, thus

giving much less time for the crystallization of the new phase to take place. On a residue leached during 6 hours and containing approximately 0.30 % of arsenic, the phase analysis showed a content of enargite and tennantite of 1.8 and 1.2 % respectively, giving an approximate arsenic content of almost 0.6 %, approximately twice as much as obtained by the chemical analysis. However, XRD analyses are subject sometimes to considerable errors depending on several factors such as the nature of the sample itself.
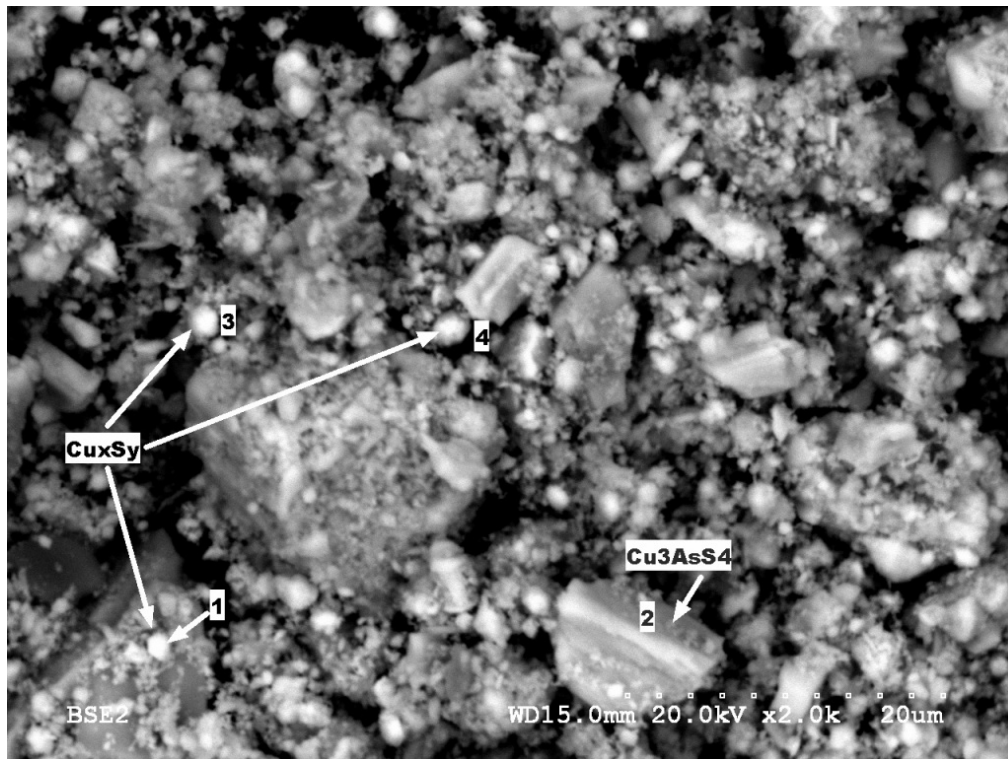
Figure 5.29: Partially leached sample. Non polished, "Enargite 2".
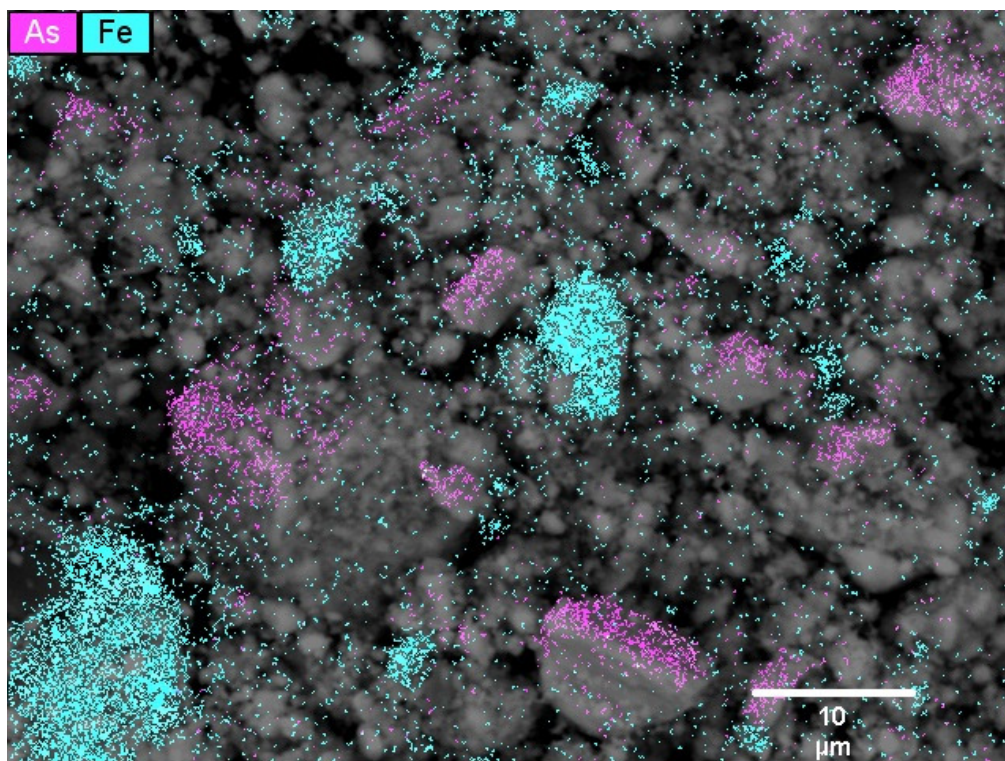
Figure 5.30: As and Fe distribution on Figure 5.26
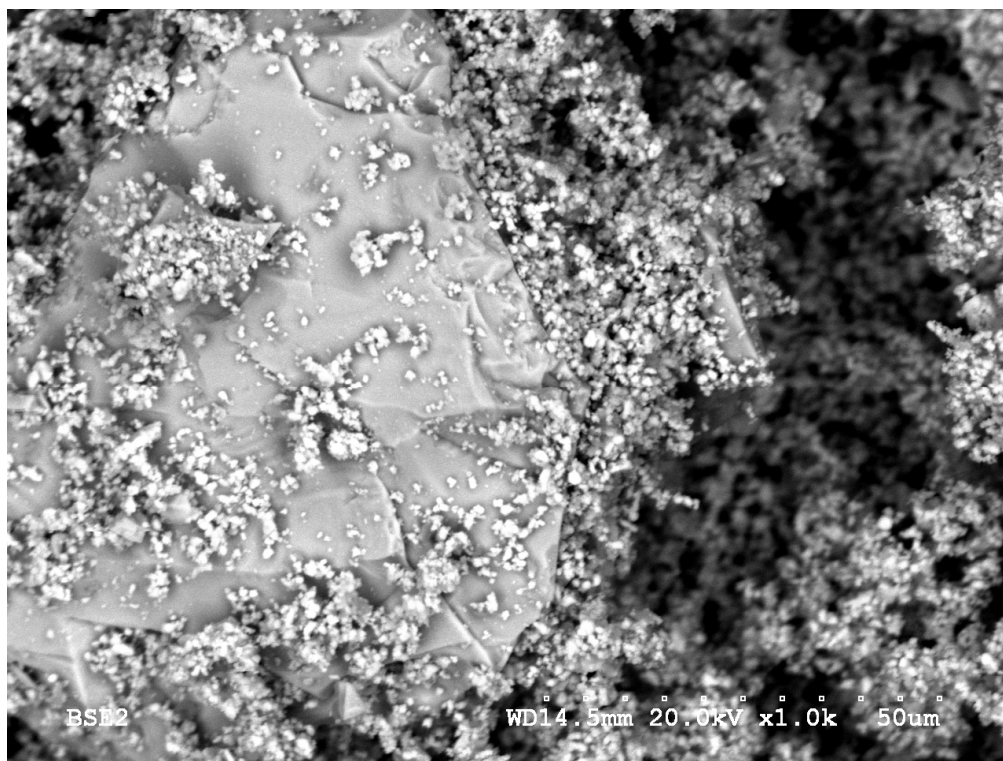
Figure 5.31: "Enargite 2" leached residue showing a large pyrite particle and the new phase formed

In the case of the leach residues, it is very likely that poor crystallization leads to the elimination of some minor phases thus increasing the content of the phases found. In regards to the new phase formed, the analysis found bornite (Cu_5FeS_4), sodium copper sulphide ($NaCu_5S_3$), digenite (Cu_9S_5) tenorite (CuO) and Chalconatronite ($Na_2Cu(CO_3)_2 \cdot 3(H_2O)$).

In order to try to improve crystallization of the new phases forming in the solid residue, a 24 hours leach test was performed on the "Enargite 2" sample. In this case sodium copper sulphide ($NaCu_5S_3$) appears to be the main new copper phase formed followed by bornite. A comparison of the head samples used and their respective solid residues can be seen in Tables 5.6 and 5.7.
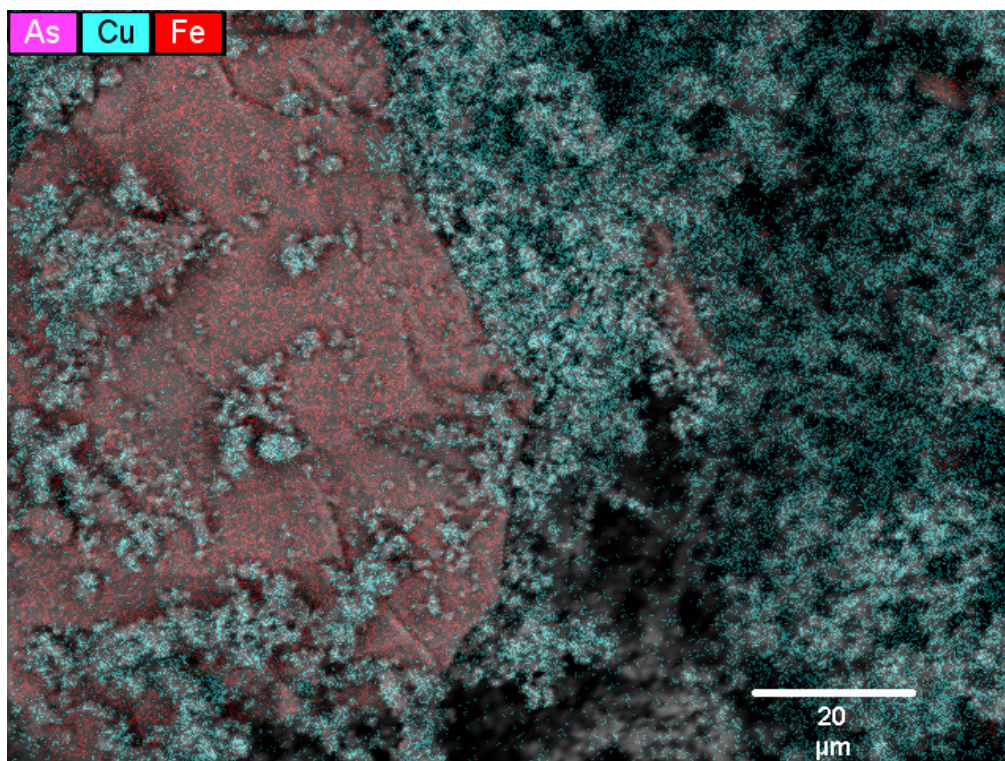
Figure 5.32: "Enargite 2" leached residue showing a large pyrite particle and the new phase formed.

Sodium copper sulphide is a chalcogenide of Na^+, Cu^+ and S^{2-} which can be synthesized by hydrothermal treatment of elemental copper in sodium sulphide solutions, and it is relevant in the superconductors field (Effenberger 1985, Starodub 1999). Its formation may be a sequence of reactions of metallic copper with sodium sulphide to form chalcocite (Cu_2S) followed by the reaction of chalcocite with sodium sulphide to form sodium copper sulphide ($NaCu_5S_3$) as shown in Equation 5.2.1. This mechanism seams feasible considering that chalcocite can be a product or an intermediate phase of the alkaline sodium sulphide leach of enargite.

$$5Cu_2S_{(s)} + NaHS_{(aq)} + NaOH_{(aq)} \Leftrightarrow 2NaCu_5S_{3(s)} + H_2O_{(l)} \qquad 5.2.1$$
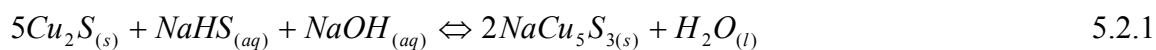
The synthesis of $NaCu_5S_3$ usually requires metallic copper and high pressure conditions, which increase its cost, however, the opportunity of using natural mineral

samples could generate some interest. Nevertheless, much more research is required to establish appropriate procedures for the production of $NaCu_5S_3$ from raw materials.

Even though the formation of $NaCu_5S_3$ could be feasible under the experimental conditions used, in some cases other copper phases were detected, such as tenorite (CuO), bornite (Cu_5FeS_4) or chalconatronite ($Na_2Cu(CO_3)_2 \cdot 3(H_2O)$). The formation of these phases is harder to explain. Tenorite could be an intermediate phase occurring in the enargite to chalcocite to sodium copper sulphide, however no literature was found. Bornite has been synthesized by different authors (Roberts 1963, Dutrizac 1973); however, at least in aqueous systems it seems that bornite could form from chalcopyrite being reacted with copper ions and there is no indication that it could form from other copper and iron sulphides such as covellite or chalcocite and pyrite. Finally chalconatronite has been reported to form under alkaline conditions reacting with CO_2 from the atmosphere (Mukhopadyhay 2004) which could explain its presence in the residues. However, as previously mentioned crystallinity of the residues was not optimal and could have led to confusing results.

Finally, a residue containing approximately 50 % of sodium copper sulphide was washed with deionized water, which led to the almost complete disappearance of the phase. The XRD pattern shows that the sodium copper sulphide peaks barely exist after the the aforementioned treatment, and give way to an amorphous phase which could be some very poorly crystallized bornite or a type of non stoichiometric copper sulphide. However, it is difficult to confirm this. Table 5.6 shows a comparison betweem "Enargite 2" head sample, its leach residues after being leached during 6 and 24 hours and a 24 hour leached residue that was washed again with deionized water. The main copper phase on this last sample is tenorite, which accounts for only 25 %, which is far from the approximately 40 % of copper expected on the residue. This can be due to the formation of amorphous phases that cannot be detected by the XRD analysis.

Table 5.6: Comparison of "Enargite 1" head sample vs. its leach residue after 24 hours of leaching

Mineral	Ideal Formula	Enargite 1 head sample	Enargite 1 leach residue
Enargite	Cu_3AsS_4	46	
Quartz	SiO_2	28.2	23.5
Pyrite	FeS_2	6.6	8
Chalcopyrite	$CuFeS_2$	5.9	4.4
Tennantite	$(Cu,Ag,Fe,Zn)_{12}As_4S_{13}$	7.8	
Galena	PbS	0.8	0.5
Dolomite	$CaMg(CO_3)_2$	1.4	
Sphalerite	$(Zn,Fe)S$	0.3	
Muscovite	$KAl_2AlSi_3O_{10}(OH)_2$	1	
Bornite	Cu_5FeS_4	2	1.9
Digenite	Cu_9S_5		53.8
Covellite	CuS		8

Table 5.7: Comparison of "Enargite 2" head sample vs. its leach residue after 6 and 24 hours of leaching

Mineral	Ideal Formula	Enargite 2 head sample	Enargite 2 leach residue 6 hours	Enargite 2 leach residue 24 hours	Enargite 2 leach residue 24 hours, washed
Enargite	Cu_3AsS_4	60.4	1.80		
Quartz	SiO_2	5.90	6.00	7.10	9.5
Pyrite	FeS_2	25.7	34.4	33.1	63.2
Tennantite	$(Cu,Ag,Fe,Zn)_{12}As_4S_{13}$	4.90	1.20		
Bornite	Cu_5FeS_4		34.2	6.40	
Digenite	Cu_9S_5		4.20		
Covellite	CuS	3.00	4.60		
Tenorite	CuO		1.70		25.6
Chalconatronite	$Na_2Cu(CO_3)_2 \cdot 3(H_2O)$		5.80		
Sodium Copper Sulphide	$NaCu_5S_3$		6.10	53.4	1.6

5.3 Arsenic precipitation

5.3.1 Precipitation by acidification

As proposed in the literature, sodium thioarsenate and sodium thioantimonate can react with acid and precipitate as sulphides (Nadkarni 1975), at the same time that hydrogen sulphide is evolved. Four different tests were performed at 95ºC on alkaline sodium sulphide solutions containing approximately 5000 ppm of arsenic and 200 ppm of antimony. Initial concentrations of sodium hydroxide and sodium sulphide were approximately 2.5 M and 1.0 M respectively.

At first, addition of acid did not produce a change in pH that could be detected by the pH probe, due to the extremely high alkalinity. Only an increase in temperature was observed. As excess hydroxide became neutralized, pH readings started to be obtained, and at a pH of approximately 8, the first yellow precipitates started to appear, but they would soon disappear. As acid addition was maintained, pH kept decreasing, however, if acid addition was stopped, pH would tend to increase again, perhaps due to evolution of hydrogen sulphide, which was especially strong below pH 7.
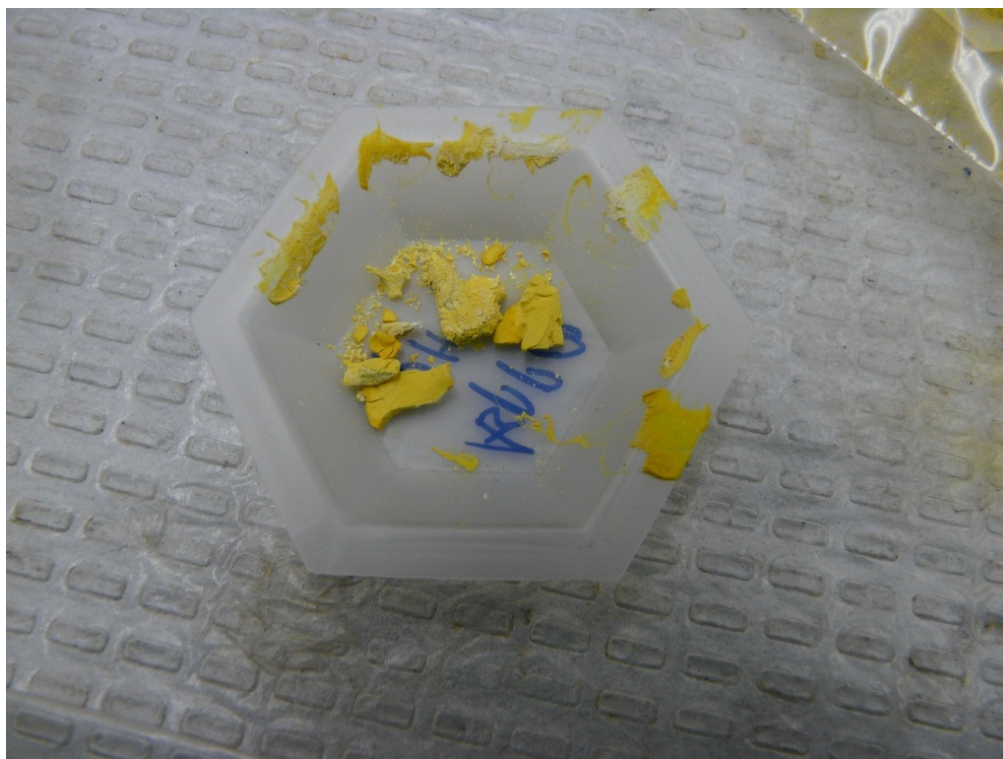
Figure 5.33: Precipitation product after acidification

Table 5.8: Main elements of interest found in precipitates after acidification

Main Elements		
As (%)	Cu (%)	Sb (%)
29.53	0.142	1.311

Table 5.9: Main phases found in precipitates after acidification

Main Phases	
Orpiment	As_2S_3
Claudetite	As_2O_3
Hydrogen Sodium Sulphate	$H_5Na(SO_4)_3$
Sodium Thiosulphate	$Na_2(S_2O_3)*5H_2O$

Finally, once the desired pH value was reached (see Table 5.10) and remained constant, the test was stopped, samples were filtered and then sent for analysis. Results indicate that practically all the arsenic and all the antimony were precipitated as a mixture of sulphides and oxides, with arsenic in the +3 state. This is in agreement with some

Pourbaix diagrams published by other researchers (Vink 1996) and with the findings of Rochette *et al* (Rochette 2000). XRD analyses detected the presence of two arsenic phases, orpiment (As_2S_3) and claudetite, (As_2O_3). The yellow precipitates present poorly crystalline structures, therefore it is possible that other phases exist that could not be detected by XRD. Figures 5.38 and 5.39 show micrographs of the precipitate samples.

Table 5.10 shows the removal of arsenic and antimony, together with the removal of sulphide from solution and reactions 5.3.1 to 5.3.6 show the proposed mechanism of orpiment precipitation from thioarsenate, which is based on the findings of Rochette (Rochette 2000).

Neutralization of sulphide with acid:

$$HS^-_{(aq)} + H^+_{(aq)} \Leftrightarrow H_2S \qquad\qquad 5.3.1$$
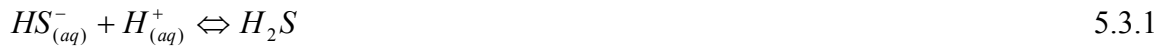
Transformation of thioarsenate to arsenate

$$AsS^{3-}_{4(aq)} + 4H_2O \Leftrightarrow AsO^{3-}_{4(aq)} + 4H_2S \qquad\qquad 5.3.2$$

Reduction of arsenate to thioarsenite or arsenite

$$4AsO^{3-}_{4(aq)} + 13H_2S \Leftrightarrow 4AsS^{3-}_{3(aq)} + H_2SO_{4(aq)} + 12H_2O \qquad\qquad 5.3.3$$

$$4AsO^{3-}_{4(aq)} + H_2S \Leftrightarrow 4AsO^{3-}_{3(aq)} + H_2SO_{4(aq)} \qquad\qquad 5.3.4$$
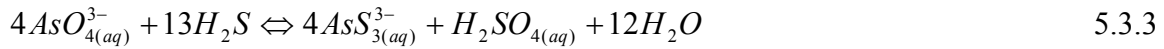
Precipitation of orpiment from thioarsenite or arsenite

$$2AsS^{3-}_{3(aq)} + 6H^+_{(aq)} \Leftrightarrow As_2S_{3(s)} + 3H_2S \qquad\qquad 5.3.5$$

$$2AsO^{3-}_{3(aq)} + 3H_2S + 6H^+_{(aq)} \Leftrightarrow As_2S_{3(s)} + 6H_2O \qquad\qquad 5.3.6$$
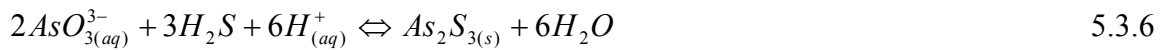
Table 5.10: Removal of As, Sb and S$^{(2-)}$ from solution during acidification

Final pH	As removal (%)	Sb removal (%)	S$^{(2-)}$ removal (%)	H$_2$SO$_4$/(As+Sb) mass ratio
2	99.93	99.98	99.49	55.98
3	99.95	99.96	99.45	45.12
4	100.0	99.98	99.27	33.29
5	99.82	99.97	98.99	26.65

Unfortunately, despite the efficient removal of arsenic and antimony from solution, as seen in Table 5.10, sulphide is also almost entirely removed, most likely as hydrogen sulphide. In fact, most of the acid goes to neutralizing sulphide and hydroxide, making its consumption too high to be considered feasible for a large scale operation.
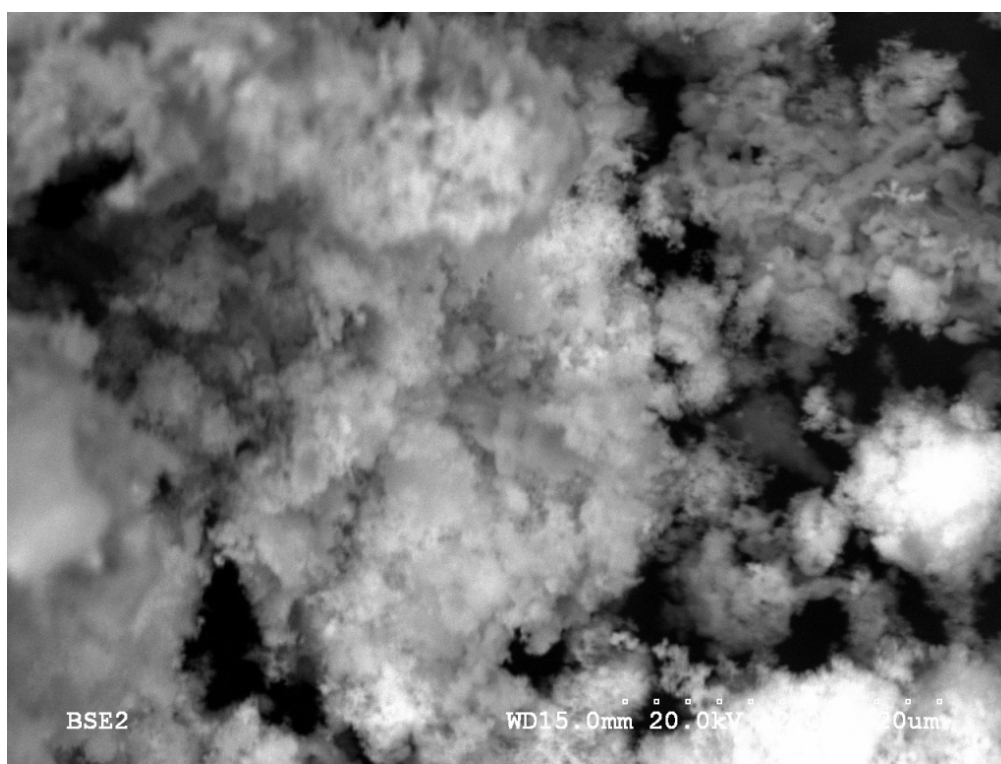
Figure 5.34: Arsenic-Antimony precipitate at pH 5.
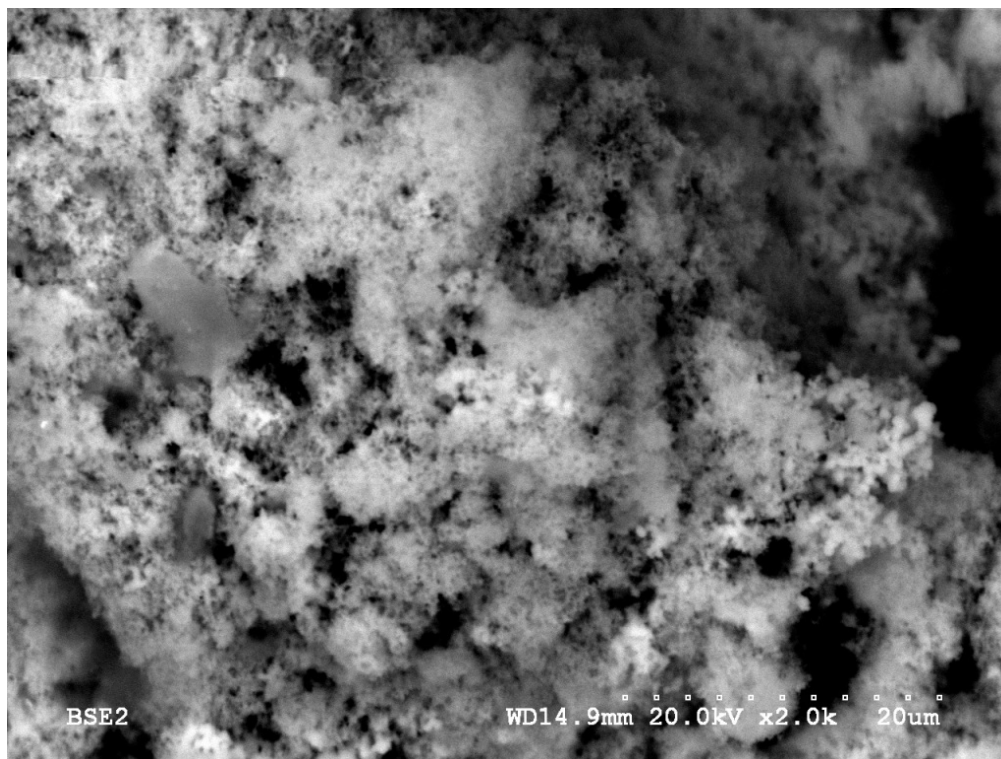
Figure 5.35: Arsenic-Antimony precipitate at pH 2

5.3.2 Crystallization of sodium thioarsenate

During the sodium sulphide leaching of enargite, arsenic and antimony are solubilised as sodium thioarsenates and thioantimonates respectively. Such compounds are said to have low solubilities at temperatures below 50ºC (Nadkarni 1988). This property makes these compounds suitable for crystallization by cooling. Nadkarni reports a removal of approximately 50 to 60 % when cooling the leach solutions overnight.

Solubility of sodium thioarsenates can be tested by leaving leach solutions to cool down for a period of time. Removal of arsenic can achieve approximately 45 %; however, antimony remains in solution due to its low content in the head sample. The crystallized samples seem to dissolve in water but not in ethanol, their appearance is white-yellow and can be easily ground in a mortar after drying.

It seems that there is still not a complete agreement among researchers as to what the arsenic behaviour is in alkaline sulphide solutions. Even though sulphide solutions are strongly reducing, arsenic (V) seems to be stable in these kinds of solutions (Rochette 2000, Stauder 2005, Wallschläger 2007). In fact, XRD analyses reveal that the crystallized compounds contain arsenate together with sodium, oxygen and sulphide at different degrees of hydration.

The literature says that ideally arsenic should be in solution as hydrated sodium thioarsenate ($Na_3AsS_4 \cdot 8H_2O$), and that it should crystallize as such (Nadkarni 1975 – 1988). However, speciation of arsenic depends on several factors such as pH, sulphide and arsenic concentration. Thioarsenates may form and include mono-, di-, tri- and tetrathioarsenate, their formulas are shown on Table 5.11 (Wallschläger 2007).

Several crystallization tests revealed that between 25 to 45 % of arsenic can be removed from solution depending apparently on the content of free sulphide and hydroxide. The precipitates were subjected to XRD analyses, which revealed the presence of arsenic (V) compounds only, suggesting that arsenic remained as arsenate in solution. The main arsenic phases found are shown in Table 5.12.

Table 5.11: List of thioarsenates (Wallschläger 2007).

Name	Formula
mono-thioarsenate	AsO_3S^{3-}
di-thioarsenate	$AsO_2S_2^{3-}$
tri-thioarsenate	$AsOS_3^{3-}$
tetra-thioarsenate	AsS_4^{3-}

Table 5.12: Main arsenic phases found in crystallized product after leaching

Main Phases	
Sodium sulphide Arsenate Hydrate	$Na_3AsO_2S_2 \cdot 11H_2O$
Sodium Sulphide Arsenate Hydrate	$Na_3AsO_2S_2 \cdot 7H_2O$
Sodium Sulphide Arsenate Hydrate	$Na_3AsS_4 \cdot 8H_2O$
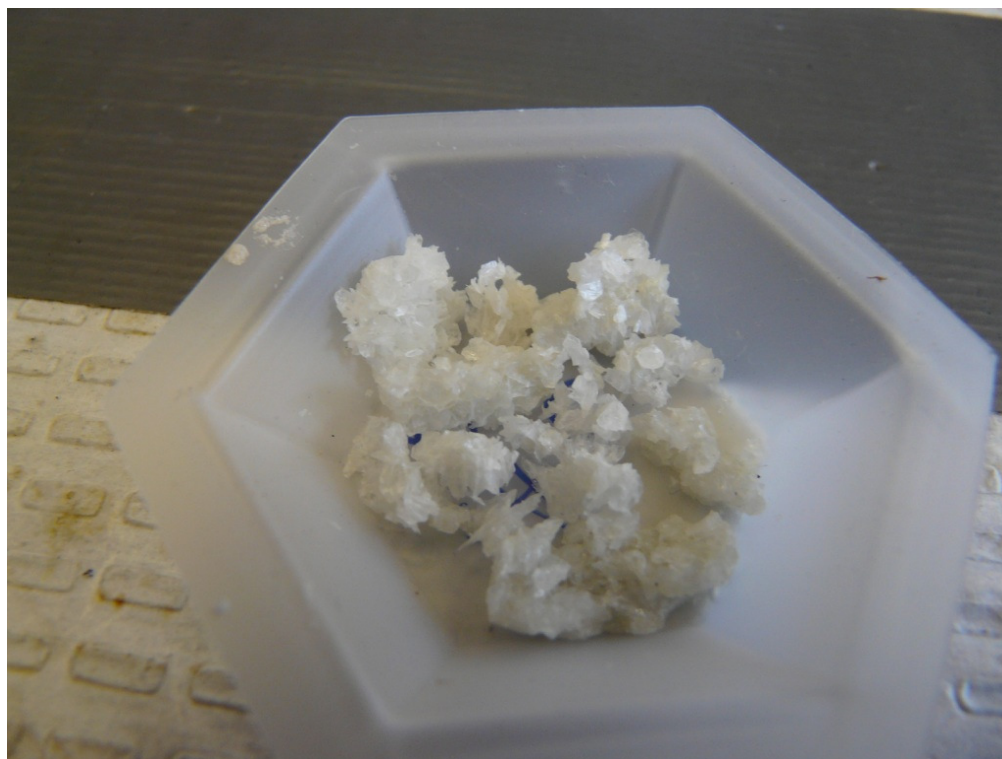
Figure 5.36: Sodium (oxy)-thioarsenate precipitates

Table 5.13: Sodium thioarsenate precipitation parameters

Precipitation parameters	As	Sb
Highest concentration seen (M)	1.30	0.032
Concentration after precipitation (M)	0.70	0.030
Content in solid precipitate (%)	11.8	0.320
Average removal from solution (%)	42.0	4.500

5.4 Leaching of chalcopyrite and pyrite

5.4.1 Atmospheric leaching of chalcopyrite

During the atmospheric alkaline sodium sulphide leaching of enargite, other copper sulphides together with a variety of metal sulphides such as iron, zinc and lead do not seem to be affected by the procedure. This, however, could change if the necessary conditions are presented, according to E. Peters (Peters 1976), who describes the theoretical decomposition of metallic sulphides in acid and alkaline solutions according to thermodynamic data, and mentions that chalcopyrite and pyrite could decompose to form solid chalcocite and magnetite at the same time that aqueous sulphide and sulphate are formed.

This idea creates an opportunity to produce aqueous sulphide in situ using minerals, thus decreasing costs. However, this does not seem to have been done in the past and E. Peters also adds that this decomposition has been seen only at high temperatures (approximately 200ºC) during the digestion of chalcopyrite in caustic soda, but these reactions are expected to be slow. Reactions 5.4.1 and 5.4.2 show the reactions proposed by Peters.

$$24CuFeS_{2(s)} + 72NaOH_{(aq)} \Leftrightarrow 12Cu_2S_{(s)} + 8Fe3O_{4(s)} + 35Na_2S_{(aq)} + 36H_2O + Na_2SO_{4(aq)} \quad 5.4.1$$

$$6FeS_{2(s)} + 24NaOH_{(aq)} \Leftrightarrow 2Fe_3O_{4(s)} + 11Na_2S_{(aq)} + Na_2SO_{4(aq)} + 12H_2O \quad\quad 5.4.2$$
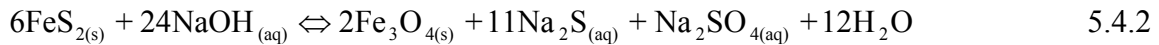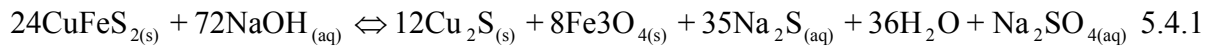
At first 10 grams of "Chalcopyrite 1" sample were leached at 95ºC in a 2.5 M sodium hydroxide solution with no sulphide and a solution with the same concentration of sodium hyhdroxide and 1 M sodium sulphide. Table 5.14 shows a comparison of the head sample and the leach residues obtained. It can be seen that apparently nothing happened to either chalcopyrite or pyrite, but other iron phases such as pyrrhotite seem to have decomposed to form sulphur and erdite or sodium thioferrate (NaFeS$_2$•2H$_2$O). The appearance of sodium thioferrate in alkaline sulphide solutions has been reported in the past (Raudsepp1981) but it was said to come from pyrite decomposition.

Table 5.14: Comparison of "Chalcopyrite 1" head sample and leach residues after 24 hours of leaching at 95°C.

Mineral	Ideal Formula	"Chalcopyrite 1" head sample	2.5 M NaOH	2.5 M NaOH, 1 M Na₂S
Chalcopyrite	$CuFeS_2$	48.6	58.0	51.2
Pyrrhotite	$Fe_{1-x}S$	35.3		24.6
Pyrite	FeS_2	8	9.8	9.2
Sulfur, elemental	S		16.3	6.7
Magnetite	Fe_3O_4	1.3	1.5	1.6
Erdite	$NaFeS_2\ 2H_2O$		7.6	2.5
Clinochlore	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$		6.8	3.6
Quartz	SiO_2	0.7		0.6

5.4.2 Leaching of chalcopyrite and pyrite at high temperature and pressure

Considering that pyrite and chalcopyrite seemed unaffected by the atmospheric leach process, autoclave leaching tests were performed at different conditions. It appears that when using low concentrations of sodium hydroxide (0.1 M), there was no considerable change from chalcopyrite or pyrite. It was only during tests performed with the addition of enargite and an initial amount of sodium sulphide in solution that production of sulphide during the leach occurred. However, this sulphide detected might come from the solubilisation of arsenic from the enargite and production of thioarsenates.

Finally, to confirm the previous results, a pyrite and a chalcopyrite sample were leached again at 220ºC for two hours but using a 2.0 M NaOH solution. After the chalcopyrite test, the solution had a yellow colour that suggests the presence of polysulphides, however, as soon as filtering started the solution became green which could probably be explained by the presence of iron. This dark green colour was apparently caused by extremely fine particles, which the next day after the test had settled to leave a clean clear solution. These fine particles may be sodium thioferrate as suggested by Raudsepp.

Also, as seen in Table 5.17, chalcopyrite seems to have decomposed to produce hematite and a different copper phase that could not be identified due probably to poor crystallinity of the new phase. The XRD spectrum shows poorly defined peaks that could suggest the presence of nanosized crystals of bornite, which could make sense according to the comments of E. Peters, who suggests that thermodynamically chalcopyrite could decompose into bornite or chalcocite at high pH. Solution analyses revealed no solubilisation any type.

On the other hand, pyrite does not seem to have been affected whatsoever by the procedure. The head sample containing approximately 95 % of pyrite increased its pyrite content to 99 % after the leach, due to the disappearance of other minor phases.

Table 5.15: Chalcopyrite autoclave leaching results when using 0.1 M NaOH and different concentrations of initial sulphide

Test	Time at 220ºC (h)	Chalcopyrite (g)	Enargite (g)	$S^{(2-)}$ in feed (mg)	Solution sample	$S^{(2-)}$ in solution (mg)	$S^{(-2)}$ produced (mg)	$S^{(2-)}$ efficiency (%)
1	1	0.0	10	4164	Blank	555.0	537.3	12.9
					Filtrate	1092		
2	1	10	10	6807	Blank	505.0	398.1	5.85
					Filtrate	903.1		
3	1	10	0	2643	Blank	0.000	39.78	1.51
					Filtrate	39.78		
4	6	10	0	2643	Blank	405.0	44.82	1.70
					Filtrate	449.8		

Table 5.16: Chalcopyrite autoclave leaching in 0.1 M NaOH results

Mineral	Ideal Formula	"Chalcopyrite 2" head sample	Test 3	Test 4
Quartz	SiO_2	11.4	10.5	0.4
Clinochlore	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$	2.4	2.5	2.8
Actinolite	$Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$	1.4		
Clinozoisite	$Ca_2Al_3(SiO_4)_3(OH)$	8.0	12.0	10.4
Analcime ?	$Na[AlSi_2O_6]\cdot H_2O$			1.4
Chalcopyrite	$CuFeS_2$	76.0	70.7	85.1
Hydronium Jarosite	$(H_3O^{1+})_2Fe_6^{3+}(SO_4)_4(OH)_{12}$	0.4		
Gypsum	$CaSO_4\cdot 2H_2O$	0.4		
Hematite	$\alpha\text{-}Fe_2O_3$		3.9	
Lepidocrocite	$\gamma\text{-}Fe^{3+}O(OH)$		0.3	

Table 5.17: Chalcopyrite and pyrite autoclave leaching in 2.0 M NaOH at 220ºC and 500 RPM of agitation velocity results

Mineral	Ideal Formula	"Chalcopyrite 2" head sample	"Chalcopyrite 2" Autoclave 2 M NaOH	"Pyrite 1" head sample	"Pyrite 1" Autoclave 2 M NaOH
Quartz	SiO_2	11.4	3.20	1.00	0.40
Clinochlore	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$	2.40	8.30		
Actinolite	$Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$	1.40			
Clinozoisite	$Ca_2Al_3(SiO_4)_3(OH)$	8.00	10.2		
Pyrite	FeS_2		4.00	95.9	99.6
Chalcopyrite	$CuFeS_2$	76.0	31.1		
Hydronium Jarosite	$(H_3O^{1+})_2Fe_6^{3+}(SO_4)_4(OH)_{12}$	0.40			
Gypsum	$CaSO_4 \cdot 2H_2O$	0.40			
Hematite	$\alpha\text{-}Fe_2O_3$		23.1		
Diopside	$CaMgSi_2O_6$		9.90		
Talc				1.60	
Melanterite	$Fe^{2+}SO_4\ 7H_2O$			1.50	
Bornite	Cu_5FeS_4		10.2		

5.5 Behaviour of arsenic (III) in alkaline sodium sulphide solutions

The disagreement found in the literature in regards to the behaviour of arsenic and antimony (III) in alkaline sulphide solutions is relevant to the sulphide leaching of enargite, especially in regards to the removal of arsenic from solution.

In order to test the potential implications that arsenic (III) could have in the leach process and precipitation process, arsenic and antimony trioxide was added to an alkaline sodium sulphide solution at 95ºC and left during 24 hours. As the material was added, it seemed to have dissolved, but soon after that, a black precipitate started to form, which was believed to be elemental arsenic and/or elemental antimony as suggested in the literature (Stauder 2005, Wallschläger 2007).

Unfortunately, XRD analyses turned out to be difficult to perform due to an apparent poor crystallinity of the black precipitate, and only elemental antimony was identified together with antimony oxide, cervantite (SbO_2) which is a mixture of Sb (III) and Sb (V), $Sb_2O_3 \cdot Sb_2O_5$. Arsenic phases were not possible to identify, even when using pure arsenic trioxide due to the poor quality of the diffraction patterns.

Since there was no precipitation of arsenic or antimony species after the black precipitate had been removed, the solution was evaporated in order to investigate if +5 species of arsenic and antimony formed as well. However, it was not possible again to obtain a useful spectra that would allow identification of the phases.

The presence of arsenic or antimony (III) during the alkaline sodium sulphide leach could lead to an increase in the content of arsenic and antimony in the final residue if they precipitate either in their elemental form or as oxides. Also, if they are capable of at least partially remaining in their +3 state in solution, this could lead to issues if the chosen procedure for removal of arsenic and/or antimony is crystallisation by cooling.

Chapter 6 Concluding remarks

- The selective leaching of arsenic and antimony using sodium sulphide in alkaline solutions is an effective way of upgrading copper-gold-silver concentrates to make them suitable for smelting. Dissolution reactions are fast, reaching under certain conditions almost 100 % removal in less than one hour without experiencing passivation.

- During the leaching process enargite releases arsenic into solution and solid copper-sulphur compounds are formed. Other metals such as zinc, iron and silver do not seem to be affected as suggested by chemical analysis of solutions and leach solid residues. The leaching reaction proposed does not seem accurate, but it serves as guidelines to describe the process. Chalcocite (Cu_2S) was not found in the residue, instead other copper sulphides appeared, which during long residence time tests may continue to react with sodium hydrosulphide to form sodium copper sulphide ($NaCu_5S_3$).

- Removal of arsenic and antimony from solution as sulphides can be done by pH control up to practically 100 %. However sulphide is also completely removed from solution and the acid consumption is rather high. Crystallization of sodium thioarsenate compounds by cooling seems to be a simpler way of removing arsenic reaching approximately 40 % removal. However, sodium thioantimonates could not be precipitated due to the low antimony content of the enargite sample used and the fact that only batch tests were performed. In a continuous process the concentration of antimony could be increased until crystallisation is possible.

- Based on the literature and on the XRD results of the crystallised samples obtained after cooling filtrate solutions, it seems that arsenic (V) is stable even in these very reducing environments.

- Filtration of the solid residues may become difficult as concentration of reagents, leaching time and pulp density is increased. As seen in the micrographs, particle size seems to decrease considerably during the leaching process, and the slurry produced after leaching can become viscous, especially with high additions of sodium sulphide and sodium hydroxide. Tests showed that leaching 200 grams of enargite sample in 200 ml of solution with approximately 100 % of the required reagents during 2 hours produced a solid residue suitable for filtering. Removal of arsenic and antimony was approximately 75 % therefore a second leaching step of the residue with a more dilute solution would be necessary. Also, the production of erdite that seemed to take place in some tests leads to serious filtration issues since it behaves like a colloid.

- The production in situ of sodium sulphide using chalcopyrite, enargite or pyrite under atmospheric conditions does not seem feasible even under high concentrations of sodium sulphide. Even in high temperature (220ºC) and high pressure conditions these minerals did not to produce any significant aqueous sulphide.

- The alkaline sodium sulphide leaching of arsenic and antimony has several advantages such as very high selectivity, relatively fast kinetics under atmospheric conditions and in cases where precious metals are present, it can be attractive for smelters. Some limitations include the inability of leaching arsenopyrite and that he process is not exothermic, unlike the high pressure leach of refractory gold ores and the volatilization of arsenic and antimony via roasting in multiple hearth furnaces or fluidized bed reactors. However, this process avoids the complexity of a high pressure reactor and will not produce volatile arsenic or antimony compounds like in a pyrometallurgical operation. Also, it can be a good alternative to roasting in smaller size operations.

Chapter 7 Recommendations for future research

- The alkaline sulphide leaching of enargite has proven to be an interesting alternative for the removal of arsenic and antimony from copper ores. Even though removal of these elements is quasi-complete, with residence times of less than 1 hour in some cases, there remain some issues. For example, the determination of conditions for optimal filterability of the leach residues and the number and conditions for batch leaching in stages would require further work.

- The composition of the solid residues can also be an area of interest. In the literature different authors report different phases formed during the leach procedure, including chalcocite, non-stoichiometric copper-sulphur compounds and jarosites. In this work new copper phases found included digenite, tenorite, bornite and sodium copper sulphide. The presence of especially this last phase can be valuable not only in the area of extractive metallurgy, but also, probably in the area of superconductors and solar cells. Determining ideal conditions for the crystallisation and stability of such phase could be considered for further research. Along with establishing the nature of the solid residue its capability of being leached as an alternative to smelting is also a relevant topic derived from this work.

- The behaviour of arsenic and antimony (III) in sulphidic solutions is still under debate. Even though several researchers suggest that arsenic (III) is not stable and disproportionates to arsenic (V) and elemental arsenic. It would be essential to confirm that the same situation takes place when using mineral samples, especially considering that the sodium sulphide leaching of tetrahedrite (Sb III) is proven technology. This issue could have implications in the crystallisation of arsenic/antimony compounds from sulphide solutions.

References

Achimovičová, M. *et al*, (1999), "Characterization of the solid residue of enargite Cu_3AsS_4 after alkaline leaching",

Ackerman, J.B. *et al*, (1993), "Hydrometallurgy at the sunshine mine metallurgical complex", Hydrometall. Proc. Milton E Wadsworth Int. Symp, 4th, 477-498

Anderson, C.G. *et al*, (1994), "Antimony separation process", US Patent number 5,290,338

Anderson, C.G. and L.G. Twidell, (2008), "The alkaline sulphide hydrometallurgical separation, recovery and fixation of tin, arsenic, antimony, mercury and gold" Lead and Zinc 2008, 121-132

Baxter, K. *et al*, (2010), "Treatment of high-arsenic copper-gold concentrates – An options review, Proceedings of Copper 2010, Copper 2010, Hamburg, Germany, 1783-1802

Biswas, A.K. and W.G. Davenport, "Extractive metallurgy of copper", Third Edition, Oxford, England, 1994.

Bluteau, M.C. and G.P. Demopoulos, (2007), "The incongruent dissolution of scorodite – Solubility, kinetics and mechanism", Hydrometallurgy, Vol. 87, 163-177.

Bothe, J.V. and P.W. Brown, (1999), "Arsenic immobilization by calcium arsenate formation", Environ. Sci. Technol., Vol. 33, 3806-3811.

Carly, R, (1980), "Procede d'elimination de l'arsenic et de l'antimoine des minerals sulfures de cuivre", French Patent

Castro, S.H. and L. Baltierra, (2005), "Study of the surface properties of enargite as a function of pH", Int. J. Miner. Process., Vol. 77, 104-115.

Castro, S., (2008), "Arsenic in the copper mining industry", Proceedings of the International Mineral Processing Congress, 24th, Beijing, China, Sept. 24-28, 1, 60-72.

Chappell, J., et al, (1995), "Speciation of arsenic in a contaminated soil by solvent extraction", Talanta, Vol. 42, No. 3, 323-329.

Coltrinari, E.L. *et al*, (1977), "Sodium sulphide leach process", US Patent number 4,052,220

Coursol, P. and N.M. Stubina, (2006), "Solid-solid reactions in the Ca3(AsSO4)2-Ca2SiO4-CaSO4 ternary system at elevated temperatures", Metallurgical and Material Transactions B, Vol. 37B, February, 141-143.

Curreli, L., *et al*, (2005), "Beneficiation of a gold bearing enargite ore by flotation and As leaching with Na-hypochlorite", Minerals Engineering, Vol. 18, 849-854.

Curreli, L. *et al*, (2009), "Arsenic leaching from a gold bearing enargite flotation concentrate", Hydrometallurgy, Vol. 96, 258-263

Dabbs, D.M. and D.C. Lynch, (1983), "Analysis of the molecular form of arsenic silicate slag" Proceedings of the 1983 Int. Sulphide Smelting Symp, San Francisco, CA, 143-170.

Davenport, W.G. *et al*, (2002), "Extractive metallurgy of copper", 4th Edition, Elsevier Science ltd.

Delfini, M. *et al*, (2003), "Arsenic leaching by Na_2S to decontaminate tailings coming from colemanite processing", Minerals Engineering, Vol. 16, 45-50

Demopoulos, G.P. *et al*, (1989), "Direct Solubilization of refractory gold by pressure chloride leaching", Extraction Metallurgy '89, IMM, London, England, 603-628.

Demopoulos, G.P. *et al*, (1995), "Precipitation of crystalline scorodite ($FeAsO_4 \cdot 2H_2O$) from chloride solutions", Hydrometallurgy, Vol. 38, 245-261.

Dreisinger, D.B. and B. Saito, (1999), "The total pressure oxidation of El Indio ore and concentrate", Proceedings of the Copper 99-Cobre 99, Int. Conf., 4th, Phoenix, Oct. 10-13, 181-195.

Dreisinger, D.B., *et al*, (2006), "Copper leaching from primary sulfides: options for biological and chemical extraction of copper", Hydrometallurgy, Vol. 83, No1-4, 10-20.

Dutrizac, J.E. and R.J.C. MacDonald, (1972), "The kinetics of dissolution of enargite in acidified ferric sulphate solutions", Canadian Metallurgical Quarterly, Vol. 11, No. 3, 469-476.

Dutrizac, J.E. and R.J.C. MacDonald, (1973), "The synthesis of some copper sulfides and copper sulfosalts in 500-700 gram quantities", Mat. Res. Bull., Vol. 8, 961-972.

Dutrizac, J.E. and J.L. Jambor, (1988), "The synthesis of crystalline scorodite, FeAsO4·2H2O", Hydrometallurgy, Vol. 19, 377-384.

Edwards, C.R, (1985), "The Equity leach plant", CIM Bulletin, Vol. 78, No 884, 84-93

Effenberger, H. and F. Pertlik, (1985) "Crystal structure of $NaCu_5S_3$", Monatshefte für Chemie, Vol. 116, 921-926.

Ferron, C.J. and W.W. Stogram, (2000), "High temperature hydrometallurgy for clean processing", Proceesings of the V Int. Conf. on Clean Tech. for the Mining Industry, Vol. II, Santiago, Chile, May 9-13, 295-305.

Filippou, D. and G.P. Demopoulos, (1997), "Arsenic immobilization by controlled scorodite precipitation", JOM, December, 52-55.

Filippou, D. *et al*, (2007), "Recovery of metal values from copper-arsenic minerals and other related resources", Mineral Processing & Extractive Metallurgy Reviews, Vol. 28, 247-298

Flynn, Jr. *et al*, (1989), "Recovery of arsenic from ores and concentrates", US Patent number 4,888,207.

Fornasiero, D., (2001), "Separation of enargite and tennantite from non-arsenic copper sulfide minerals by selective oxidation or dissolution", International Journal of Mineral Processing, Vol. 61, No. 2, 109-119.

Fujita, T. *et al*, (2008), "Novel atmospheric scorodite synthesis by oxidation of ferrous sulfate solution. Part I", Hydrometallurgy, Vol. 90, 92-102.

Fujita, T. *et al*, (2008), "Effects of zinc, copper and sodium ions on ferric arsenate precipitation in a novel atmospheric scorodite process", Hydrometallurgy, Vol. 93, 30-38.

Fujita, T. *et al*, (2009), "Effect of pH on atmospheric scorodite synthesis by oxidation of ferrous ions: Physical properties and stability of the scorodite", Hydrometallurgy, Vol. 96, 189-198.

Fullston, D. *et al*, (1999), "Zeta potential study of the oxidation of copper sulfide minerals", Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 146, 113-121.

Gajam, S. and S. Raghavan, (1983), "A kinetic study of enargite dissolution in ammoniacal solutions", Int. J. of Mineral Processing, Vol. 10, No. 2, March, 113-129.

Giggenbach, W, (1971), "Optical spectra of highly alkaline sulfide solutions and the second dissociation constant of hydrogen sulfide", Inorganic Chemistry, Vol. 10, No. 7, 1333-1338

Guo, H. and W.-T. Yen, (2002), "Surface potential and wettability of enargite in potassium amyl xanthate solution", Minerals Engineering, Vol. 15, 405-414.

Guo, H. and W.-T. Yen, (2005), "Selective flotation of enargite from chalcopyrite by electrochemical control", Minerals Engineering, Vol. 18, 605-612.

Hasegawa, H., et al, (1994), "Speciation of arsenic in natural waters by solvent extraction and hydride generation atomic absorption", Anal. Chem, Vol. 66, 3247-3252.

Herreros, O., et al, (2002), "Dissolution kinetics of enargite in dilute Cl_2/Cl^- media", Hydrometallurgu. Vol. 64, 153-160.

Holmes W.C. et al, (1943), "Electrolytic recovery of metals, US Patent number 2,331,395

Holmes W.C. et al, (1973), "Process for removal of arsenic from sulfo-ore", US Patent number 3,709,680.

Hopkin, W., (1989), "The problem of arsenic disposal in non ferrous metals production", Environ. Geochem. Health, Vol. 11, 101-112.

Hourn, M.M. et al, (1999), "Atmospheric mineral leaching process", US Patent number 5,993,635.

Itagaki, K. and A Yazawa, (1983), "Thermodynamic evaluation of distribution behaviour of arsenic, antimony and bismuth in copper smelting", Proceedings of the 1983 Int. Sulfide Smelting Symp, San Francisco, CA, 119-142,

Jones, H. et al, (2008), "Case reports: arsenic pollution in Thailand, Bangladesh and Hungary", Reviews of environmental contamination and toxicology, Vol 197, 163-187.

Ke, Jia-Jun and Rui-Yun Qin, (2000), "Arsenic removal and Bismuth recovery from copper smelter flue dust", Processing and environmental aspects of As, Sb, Te and Bi (Symposium), Salt Lake City, UT, USA, 293-298.

Krause, E. and V.A. Ettel, (1989), "Solubility and stability of ferric arsenate compounds", Hydrometallurgy, Vol. 22, 311-337.

Langmuir, D. *et al*, (2006), "Solubility products of amorphous ferric arsenate and crystalline scorodite (FeAsO$_4$·2H$_2$O) and their application to arsenic behavior in buried mine tailings", Geochimica et Cosmochimica Acta, Vol 70, 2942-2956.

Licht, S, (1988), "Aqueous solubilities, solubility product and standard oxidation-reduction potentials of the metal sulfides", J. Electrochemical Society: Electrochemical science and technology, Vol. 135, No. 12, 2971-2975.

Lindkvist, G. and Å. Holmström, (1983), `"Roasting of complex concentrates with high arsenic content", Proceedings of the 1983 Int. Sulfide Smelting Symp, San Francisco, CA, 451-473.

Ma, X. and W.J. Bruckard, (2009), "Rejection of arsenic minerals in sulfide flotation – A literature review", Int. J. Miner. Process., Vol. 93, 89-94.

Madsen, B.W. *et al*, (1983), "Recovery of arsenic from flue dust", US Patent number 4,401,632.

Mandal, B.K. and K.T. Suzuki, (2002), "Arsenic round the world: a review", Talanta, Vol. 58, 201-235.

Mayhew, K., *et al*, (2010), "CESL process as applied to enargite-rich copper concentrates", Proceedings of Copper 2010, Hamburg, Germany, 1983-1998.

Mihajlovic, I., *et al*, (2007), "A potential method for arsenic removal from copper concentrates", Minerals Engineering, Vol. 20, 26-33.

Monhemius, A.J. and P.M. Swash, (1999), "Removing and stabilizing As from copper refining circuits by hydrothermal processing", JOM, September 1999, 30-33.

Mukhopadyhay, U. and I. Bernal, (2004), "A totally unexpected synthesis of single crystals of the mineral chalconatronite, Na$_2$[Cu(CO$_3$)$_2$]•3H$_2$O, from a solution of a copper coordination compound and atmospheric CO$_2$, at room temperature.

Musu, E., *et al*, (2009), "The reaction of enargite with alkaline NaClO solutions: an AFM and flow-through study", Eur. J. Mineral., Vol 21, 193-202.

Nadkarni R.M. *et al*, (1975), "Method for removing arsenic and antimony from copper ore concentrates", US Patent number 3,911,078

Nadkarni, R.M and C.L. Kusik, (1988), "Hydrometallurgical removal of arsenic from copper concentrates", Arsenic Metallurgy Fundam. Appl. Proc. Symp, 263-286

Nakazawa, S. *et al*, (1999), "Simulation of the removal of arsenic during the roasting of copper concentrate", Metallurgical and Materials Transactions B, Vol. 39B, June 1999, 393-401.

Nishimura, T. and Y. Umetsu, (2000), "Chemistry on elimination of arsenic, antinomy, and selenium from aqueous solution with iron(III) species", Minor Elements 2000, CA, Young (editor), Soc. Met. Expl., Littleton, CO, USA, 105-112.

Oyarzun, R. *et al*, (2004), "Strong arsenic enrichment in sediments from the Elqui watershed, Northern Chile: industrial (gold mining at El Indio – Tambo district) vs. geologic processes", Journal of Geochemical Exploration, Vol. 84, 53-64.

Oyarzun, R. *et al*, (2006), "The As-contaminated Elqui river basin: a long lasting perspective (1975-1995) covering the initiation and development of Au-Cu-As mining in the high Andes of Northern Chile", Enirong. Geochem. Health, Vol. 28, 431-443.

Papassiopi, N. *et al*, 1996, "Removal and fixation of arsenic in the form of ferric arsenates. Three parallel experimental studies", Hydrometallurgy, Vol. 41, 243-253.

Padilla, R. *et al*, (2001), "Decomposition of enargite in nitrogen atmosphere", Canadian Metallurgical Quarterly, Vol. 40, No. 3, 335-342.

Padilla, R. *et al*, (2005), "Leaching of enargite in H_2SO_4 – NaCl – O2 media", Hydrometallurgy, Vol. 80, 272-279.

Padilla, R. *et al*, (2008), "Kinetics of pressure dissolution of enargite in sulfate-oxygen media", Metallurgical and Materials Transactions B, Vol. 39B, June, 399-407.

Papangelakis, V.G. and G.P. Demopoulos, (1990), "Acid pressure oxidation of arsenopyrite: Part I, reaction chemistry", Candian Metallurgical Quarterly, Vol. 29, 1-11.

Papassiopi, N. *et al*, (1996), "Removal and fixation of arsenic in the form of ferric arsenates. Three parallel experimental studies", Hydrometallurgy, Vol. 41, No. 2-3, 243-253

Peters, E., (1976), "Direct leaching of sulfides: Chemistry and applications", Metallurgical Transactions B, Vol. 7B, December, 505-517.

Protopopoff, E. and P. Marcus, (2003), "Potential-pH diagrams for sulphur and hydroxyl adsorbed on copper surfaces in water containing sulfides, sulfites or thiosulfates", Corrosion Science, Vol. 45, 1191-1201

Raudsepp, R, (1981), "The alkaline sulphide leaching of tetrahedrite concentrate", MASc Thesis, The University of British Columbia

Reynolds, J.E., *et al*, (1981), "Process for recovering metal values from materials containing arsenic", US Patent number 4,244,734.

Rivera, B.F. and D.G. Dixon, (2009), "Lixiviando concentrados de cobre con alto contenido de arsenico", XXIX Mining Convention, The Peruvian Institute of Mining Engineers, Arequipa, Peru, September 2009.

Riveros, P.A. *et al*, (2001), "Arsenic disposal practices in the metallurgical industry", Canadian Metallurgical Quarterly, Vol. 40, No. 4, 395-420.

Riveros, P.A. and J.E. Dutrizac, (2008), "The leaching of tennantite, tetrahedrite and enargite in acidic sulphate and chloride media", Canadian Metallurgical Quarterly, Vol. 47, No. 3, 235-244.

Roberts, W.M.B., (1963), "The low temperature synthesis in aqueous solution of chalcopyrite and bornite", Economic Geology, Vol. 58, 52-61.

Robins, R.G. *et al*, (1988), "The adsorption of arsenate ion by ferric hydroxide", Arsenic Metallurgy Fundamentals and Applications, R.G. Reddy, J.L. Hendrix and P.B. Queneau (editors), The Minerals, Metals and Materials Society, Warrendale, PA, U.S.A., 99-112.

Robles, A. *et al*, (1999), "Alkaline arsenic leaching from smelter flue dust and leaching solution regeneration", Proceedings of the Copper 99-Cobre 99, Int. Conf., 4th, Phoenix, Oct. 10-13, Vol. VI, 261-272.

Rochette, E.A. *et al*, (2000), "Kinetics of arsenate reduction by dissolved sulfide", Environ. Sci. Technology, Vol. 34, 4714-4720.

Senior, G.D. *et al*, (2006), "The selective flotation of enargite from other copper minerals – a single mineral study in relation to beneficiation of the Tampakan deposit in the Philippines", Int. J. Miner. Process., Vol. 81, 15-26.

Shalabh Singhania *et al*, (2005), Temperature and seeding effects on the precipitation of scorodite from sulfate solutions under atmospheric pressure conditions", Metallurgical and Materials Transactions B, Vol 36B, June, 327-333.

Starodub, V.A., (1999), "Ternary and quaternary chalcogenides of group IB elements", Russian Chemical Reviews, Vol. 68, No. 10, 801-820.

Stauder, S. *et al*, (2005), "Thioarsenates in sulfidic waters", Environ. Sci. Technol., Vol. 39, 5933-5939.

Stichbury, M.L. *et al*, (2000), "Microbially-mediated reductive dissolution of arsenic bearing minerals in a gold mine tailings impoundment", ICARD 2000, Fifth International Conference on Acid Rock Drainage, Soc. Min. Met. Expl., Littleton, CO, U.S.A., 97-103.

Swash, P.M. and A.J. Monhemius, (1995), "Synthesis, characterization and solubility testing of solids in the Ca-Fe-AsO$_4$ system", Sudbury '95 – Mining and the Environment, 1995, T.P. Hynes and M.C. Blanchette (editors), CANMET, Ottawa, Canada, 17-28.

Swelund, P.J. and J.G. Webster, (1999), "Adsorption and polymerization of silicic acid on ferrihydrite, and its effect on arsenic adsorption", Wat. Res, Vol. 33, No. 16, 3413-3422.

Tongamp, W. *et al*, (2009), "Arsenic removal from copper ores and concentrates through alkaline leaching in NaHS media", Hydrometallurgy, Vol. 98, 213-218

Tongamp, W. *et al*, (2010), "Selective leaching of arsenic from enargite in NaHS-NaOH media", Hydrometallurgy, Vol. 101, 64-68

Twidell, L.G. and A.K. Mehta, (1985), "Disposal of arsenic bearing copper smelter flue dust", Nuclear and chemical waste management, Vol. 5, 297-303.

Twidell, L.G. *et al*, (1999), "Technologies and potential technologies for removing arsenic from process and mine water", Rewas'99, Global Symposium on Recycling, Waste treatment and Clean Technology, 1999, I. Gaballah, J.P. Hager and R. Solozabal (editors), The Minerals, Metals and Materials Society, Warrebdale, PA, U.S.A., 1715-1726.

Valenzuela, A. *et al*, (2000), "Arsenic management in pyrometallurgical processes. Part I: Distribution in smelting/converting", Environmental Improvements in Mineral

Processing and Extractive Metallurgy, proceedings of the V International Conference on Clean Technologies for the Mining Industry, Santiago, Chile, 95-105.

Valenzuela, A. *et al*, (2000), "Arsenic management in pyrometallurgical processes. Part II: Recovery and disposal", Environmental Improvements in Mineral Processing and Extractive Metallurgy, proceedings of the V International Conference on Clean Technologies for the Mining Industry, Santiago, Chile, 107-121

Vink, B.W., (1996), "Stability regions of antimony and arsenic compounds in the light of revised and extended Eh-pH diagrams", Chemical Geology, Vol. 130, 21-30.

Viñals, J *et al*, (2003), "Topochemical transformation of enargite into copper oxide by hypochlorite leaching", Hydrometallurgy, Vol. 68, 183-193.

Viñals, J. *et al*, (2010), "Arsenic inertization from copper pyrometallurgy through phases of the alunite supergroup", Proceedings of Copper 2010-Cobre 2010, Hamburg, Germany, 2071-2086.

Wallschläger, D. *et al*, (2007), "Determination of (oxy)thioarsenates in sulfidic waters", Anal. Chem., Vol. 79, 3873-3880.

Waltman, C.A. and M.J. Eick, (2002), "Kinetics on goethite in the presence of sorbed silicic acid, Soil Sci. Soc. Am. J., Vol. 66, 818-825.

Welham, N.J. *et al*, (2000), "The stability of iron phases presently used for disposal from metallurgical systems – A review", Minerals Engineering, Vol. 13, No. 8-9, 911-931.

Wilkomirsky, I. *et al*, (2008), "A smelter reactor to treat copper concentrates with high arsenic content", Chilean Patent Application No. 3350-2008.

Wilkomirsky, I. *et al*, (2010), "Smelting of high-arsenic copper concentrates", Proceedings of Copper 2010, Copper 2010, Hamburg, Germany, 1273.

Zhang, W. *et al*, (1988), "Leacihng and recovery of arsenic from smelter fume", Proceedings of the Int. Symp. On Waste Processing and Recycling in Mineral and Metallurgical Industries, 3rd, Calgary, Alberta, August 16-19, 259-271.

Zhao, Jianmin *et al*, (1994), "Ferrihydrite: surface structure and its effects on phase transformation", Clays and Clay Minerals, Vol. 42, No. 6, 737-746.

Other sources:

London Metal Exchange website; www.lme.co.uk

Infomine website; www.infomine.com

Appendices

Appendix A

"Enargite 1" and "Enargite 2", head sample and leach residues; SEM micrographs, EDX and XRD analyses including spectra.
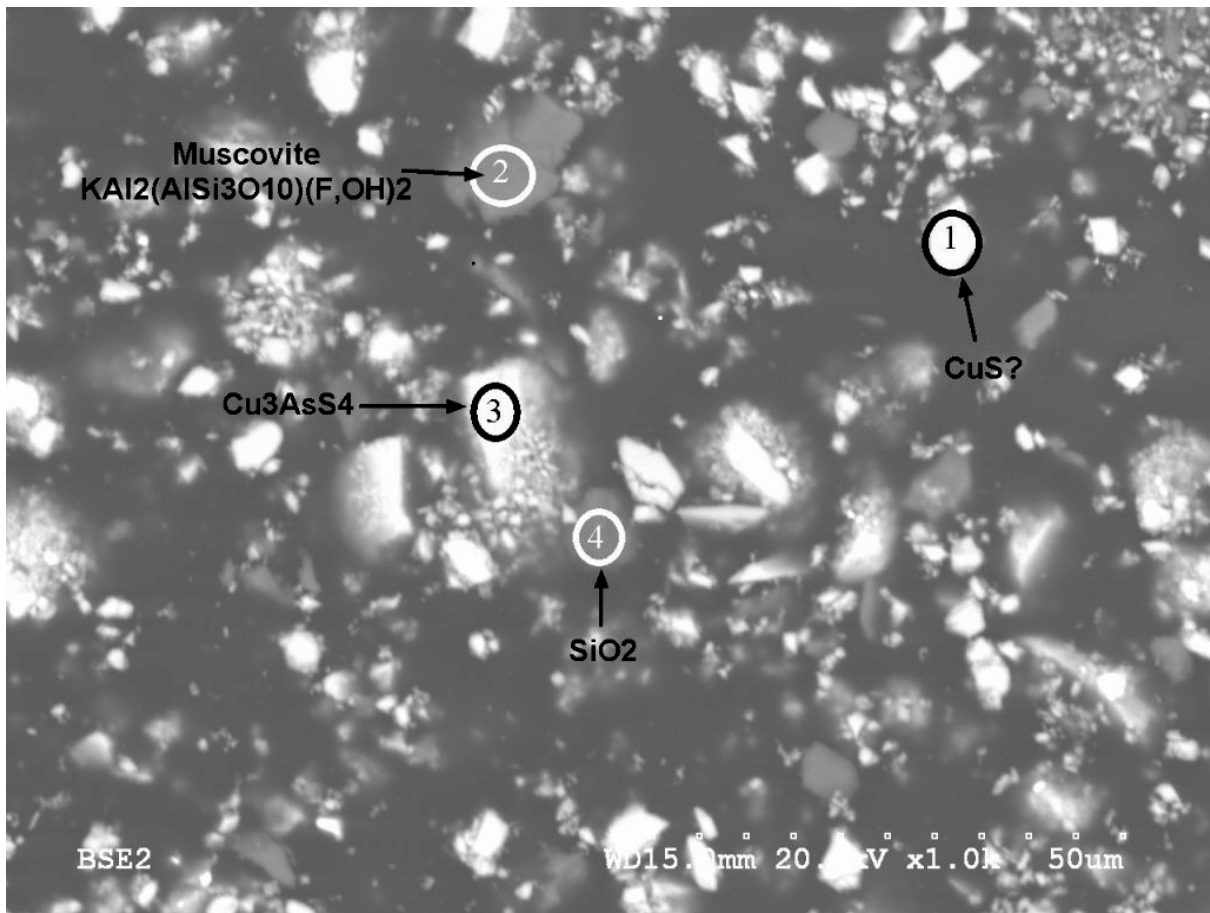
Figure A- 1: "Enargite 1" head sample SEM micrograph.

Table A- 1: EDX analysis of "Enargite 1" head sample, circled area 1.

Element	Concentration	
Oxygen	10.61 at%	3.71 wt%
Silicon	1.62 at%	0.99 wt%
Sulfur	37.15 at%	26.05 wt%
Iron	8.10 at%	9.90 wt%
Copper	41.45 at%	57.61 wt%
Arsenic	1.07 at%	1.75 wt%
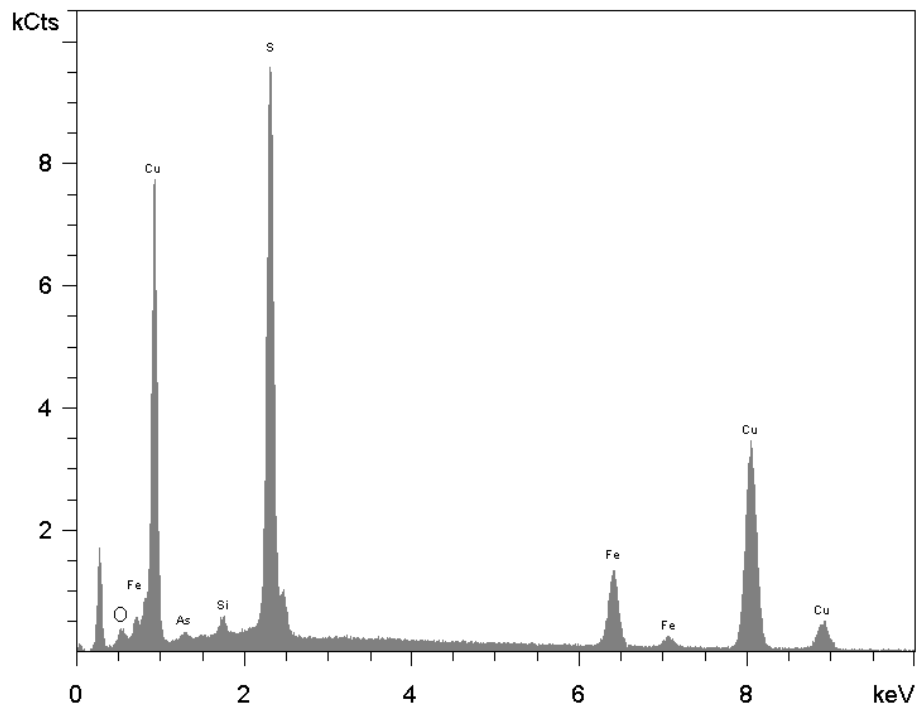
Figure A- 2: EDX analysis of "Enargite 1" head sample, circled area 1.

Table A- 2: EDX analysis of "Enargite 1" head sample, circled area 2.

Element	Concentration	
Oxygen	62.50 at%	47.05 wt%
Sodium	0.44 at%	0.48 wt%
Magnesium	0.69 at%	0.79 wt%
Aluminum	13.56 at%	17.22 wt%
Silicon	16.09 at%	21.27 wt%
Sulfur	1.35 at%	2.04 wt%
Potassium	4.22 at%	7.76 wt%
Iron	0.15 at%	0.39 wt%
Copper	1.00 at%	3.00 wt%
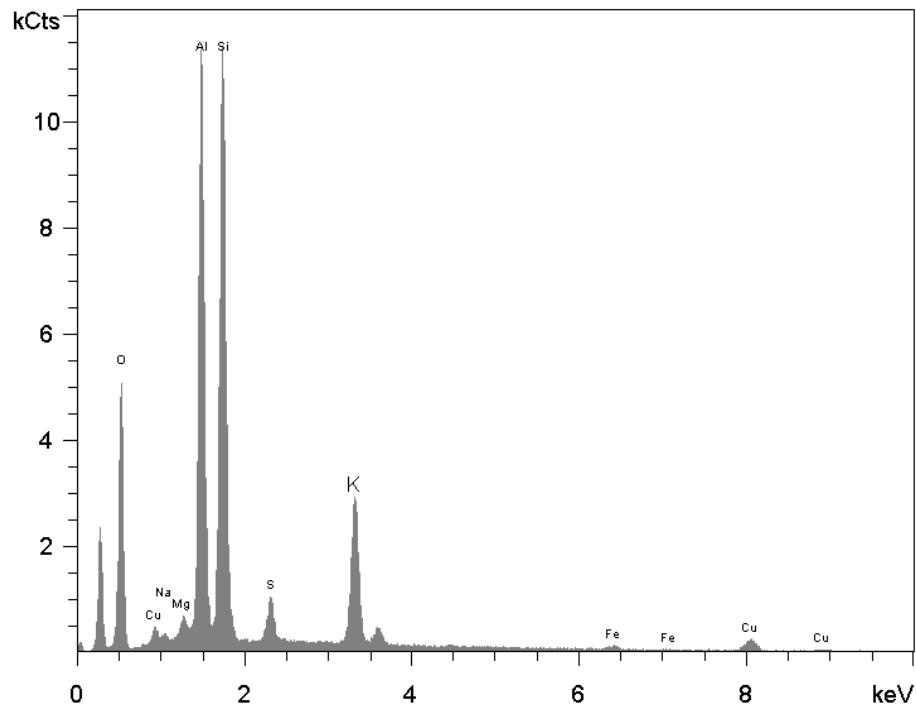
Figure A- 3: EDX analysis of "Enargite 1" head sample, circled area 2.

Table A- 3: EDX analysis of "Enargite 1" head sample, circled area 3.

Element	Concentration	
Oxygen	11.75 at%	4.21 wt%
Silicon	1.75 at%	1.10 wt%
Sulfur	44.08 at%	31.67 wt%
Iron	0.32 at%	0.40 wt%
Copper	31.63 at%	45.04 wt%
Arsenic	10.47 at%	17.58 wt%
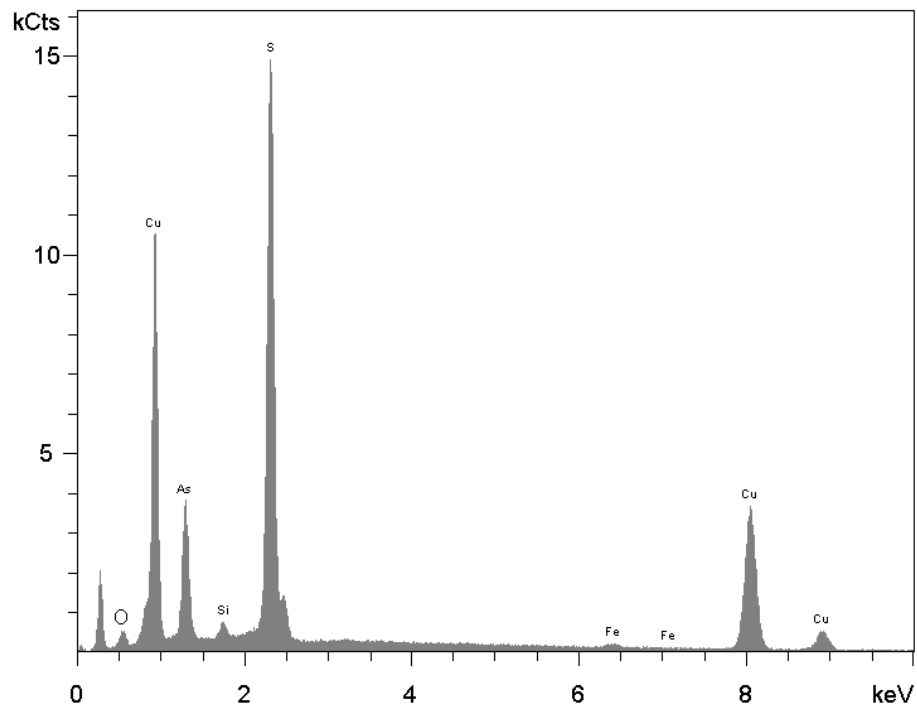
Figure A- 4: EDX analysis of "Enargite 1" head sample, circled area 3

Table A- 4: EDX analysis of "Enargite 1" head sample, circled area 4.

Element	Concentration	
Oxygen	61.40 at%	44.84 wt%
Aluminum	0.91 at%	1.12 wt%
Silicon	30.60 at%	39.23 wt%
Sulfur	4.04 at%	5.91 wt%
Calcium	0.15 at%	0.28 wt%
Iron	0.28 at%	0.72 wt%
Copper	2.07 at%	6.00 wt%
Arsenic	0.55 at%	1.89 wt%
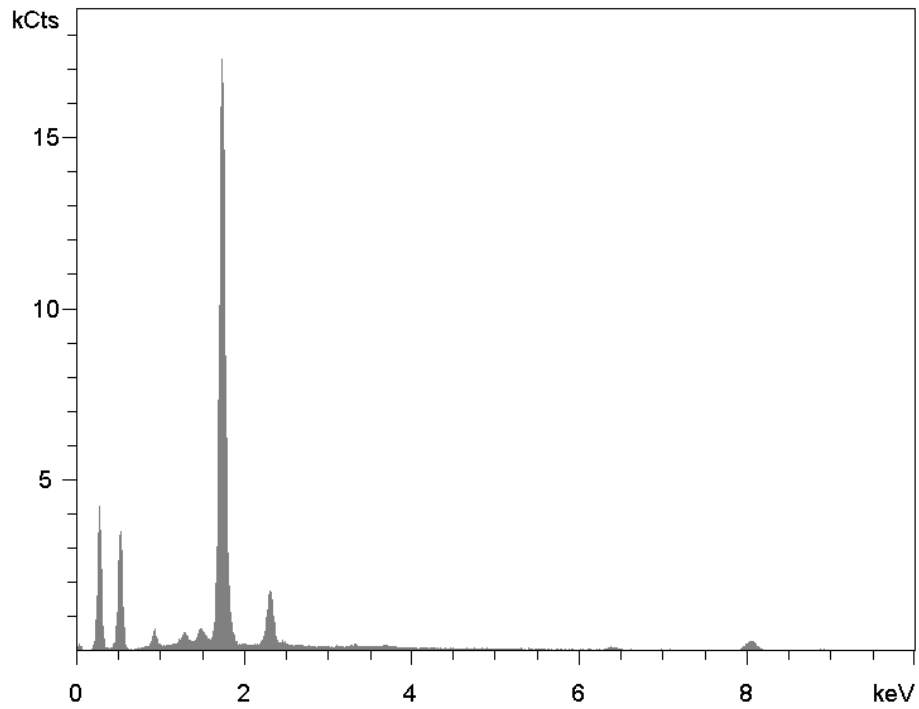
Figure A- 5: EDX analysis of "Enargite 1" head sample, circled area 4.
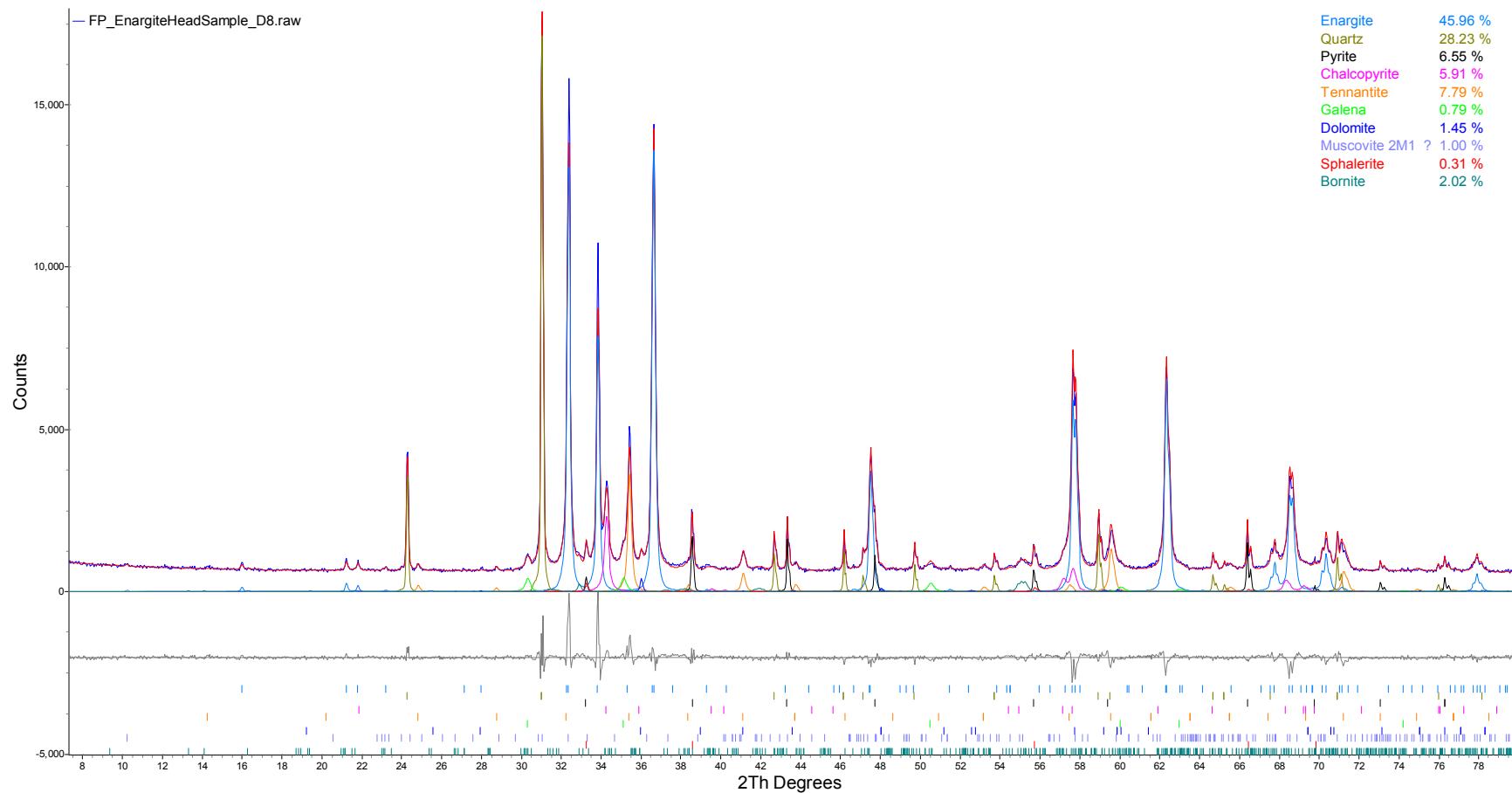
Figure A- 6: Rietveld refinement plot of "Enargite 1" head sample (blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases.
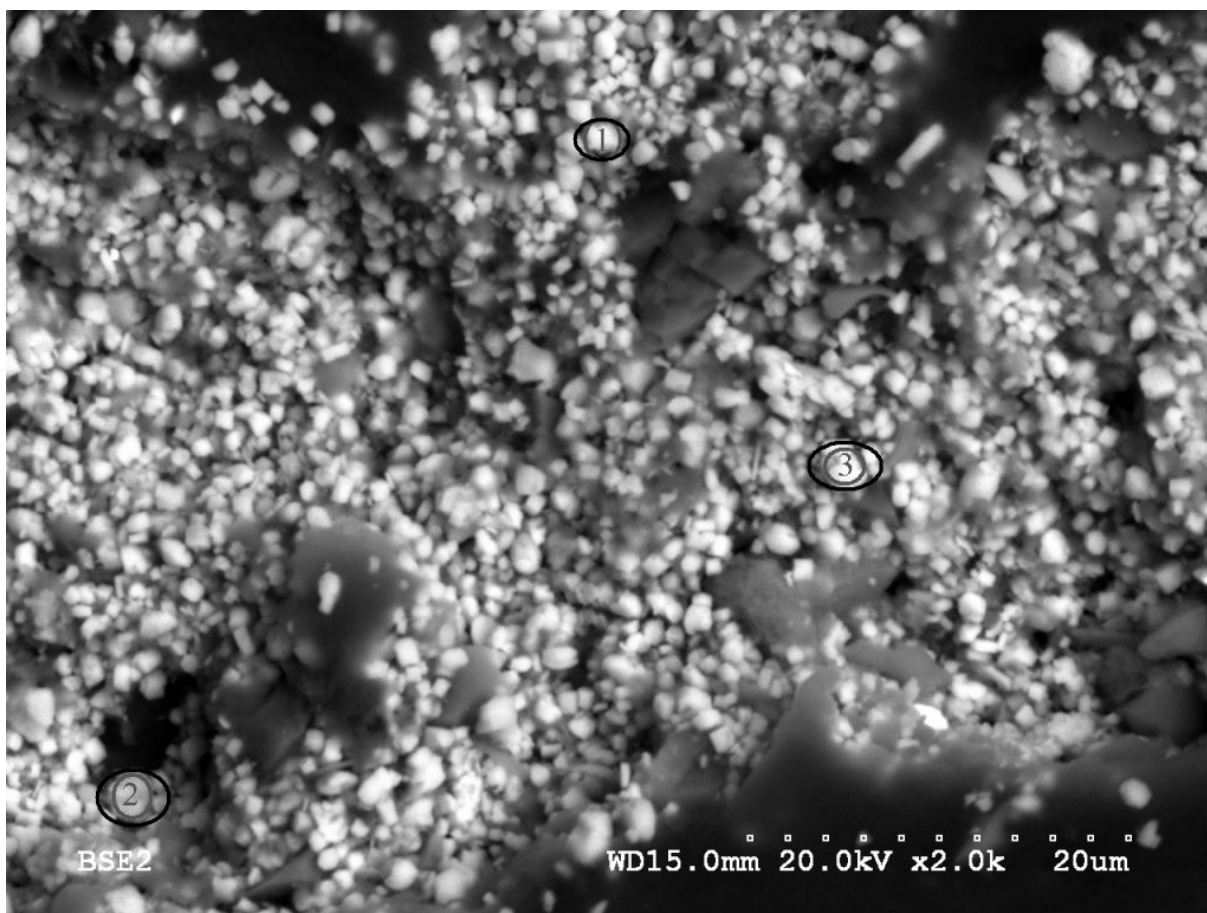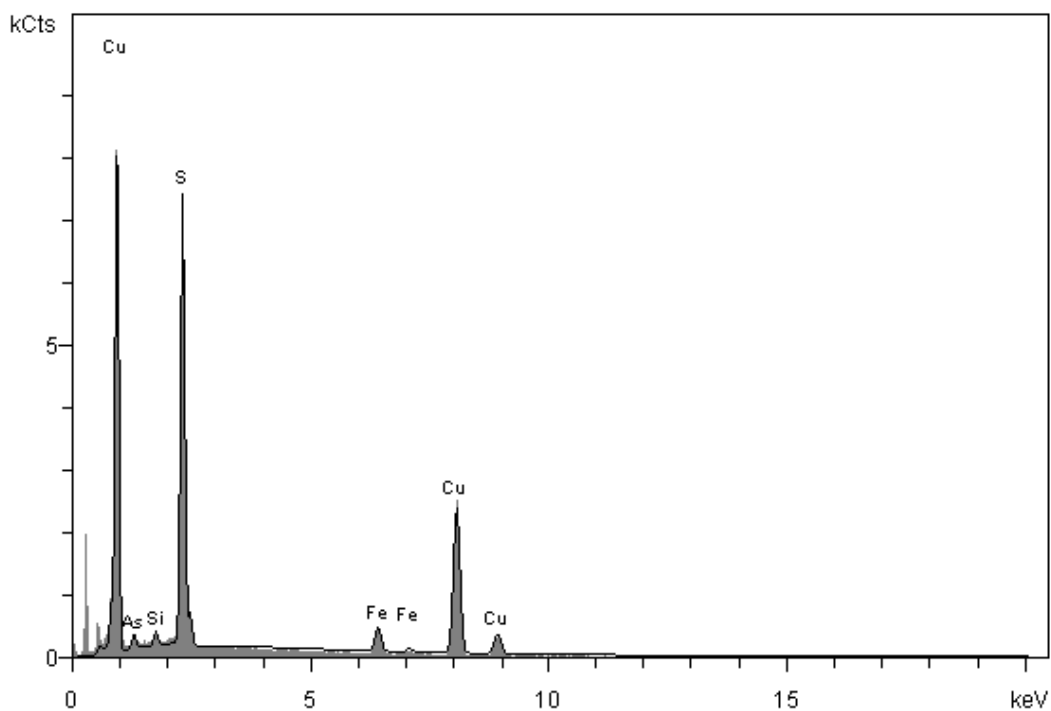
Figure A- 7: "Enargite 1" sample after leaching during 1 hour in 2.5 M NaOH and 1.0 M Na$_2$S.

Table A- 5: EDX analysis of "Enargite 1" sample after leaching during 1 hour in 2.5 M NaOH and 1.0 M Na₂S circled area 1.
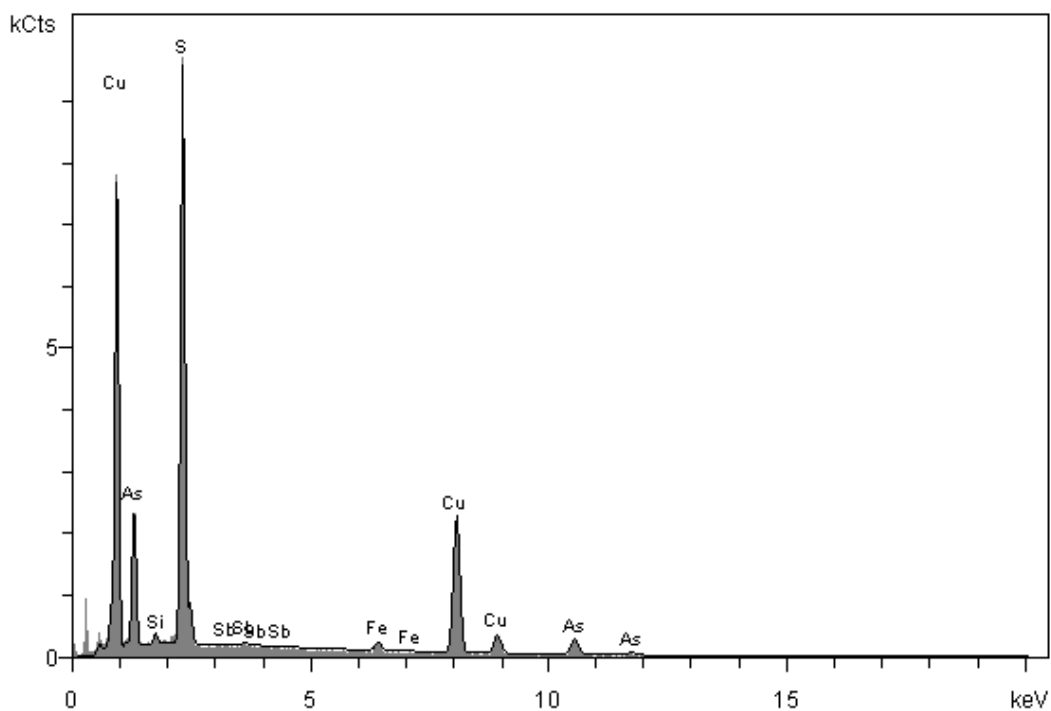
| Element	Concentration	
Oxygen	26.29 at%	10.19 wt%
Silicon	3.20 at%	2.17 wt%
Sulfur	27.71 at%	21.52 wt%
Iron	0.95 at%	1.28 wt%
Copper	40.53 at%	62.38 wt%
Arsenic	1.07 at%	1.94 wt%
Rubidium	0.25 at%	0.53 wt%
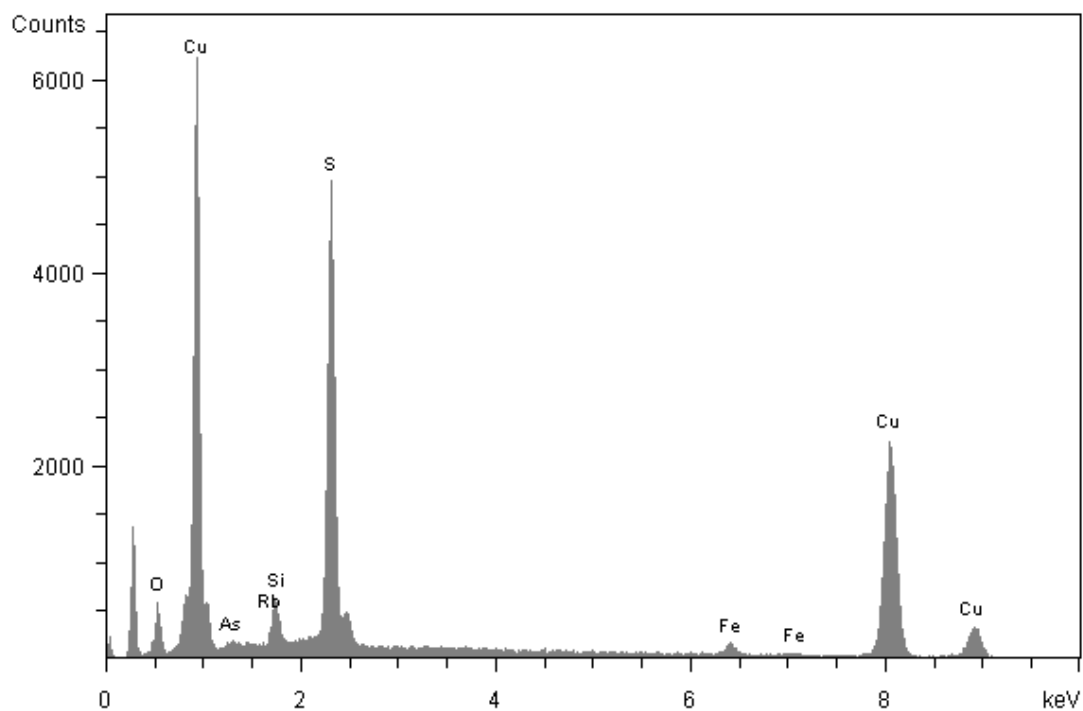
Figure A- 8: EDX analysis of "Enargite 1" sample after leaching during 1 hour in 2.5 M NaOH and 1.0 M Na₂S circled area 1.

Table A- 6: EDX analysis of "Enargite 1" sample after leaching during 1 hour in 2.5 M NaOH and 1.0 M Na₂S circled area 2.

| Element	Concentration	
Carbon	67.52 at%	41.39 wt%
Oxygen	14.48 at%	11.83 wt%
Aluminum	0.06 at%	0.08 wt%
Silicon	0.40 at%	0.57 wt%
Sulfur	6.57 at%	10.75 wt%
Iron	0.58 at%	1.66 wt%
Copper	10.40 at%	33.72 wt%
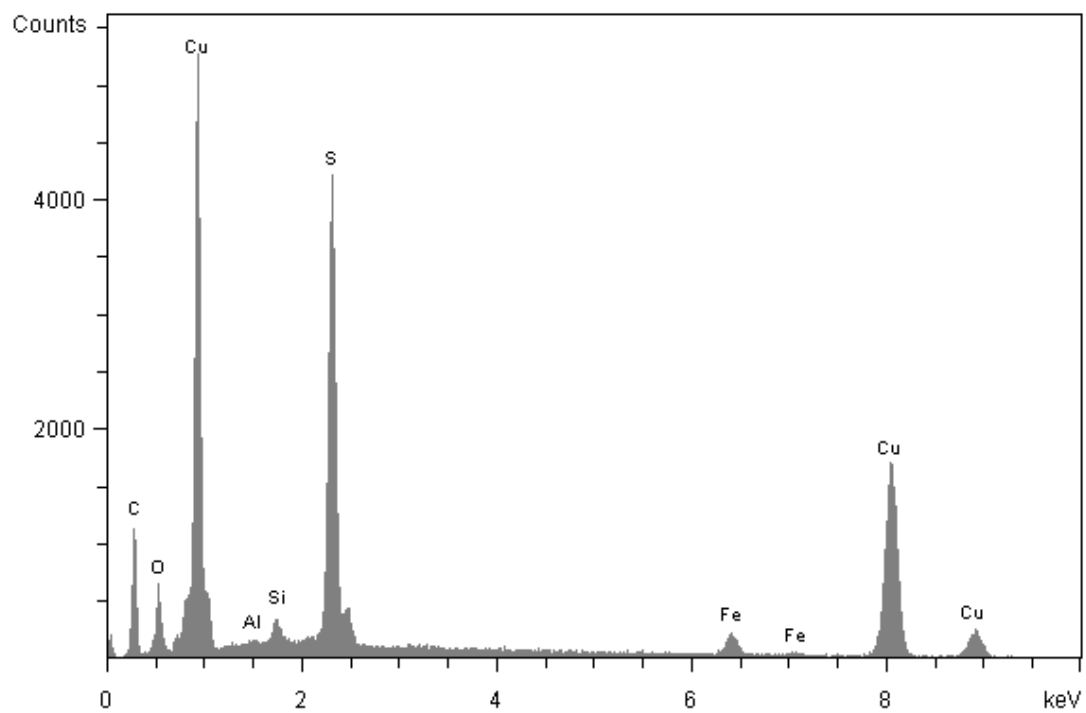
Figure A- 9: EDX analysis of "Enargite 1" sample after leaching during 1 hour in 2.5 M NaOH and 1.0 M Na₂S circled area 2.

Table A- 7: EDX analysis of "Enargite 1" sample after leaching during 1 hour in 2.5 M NaOH and 1.0 M Na₂S circled area 3.

| Element	Concentration
Oxygen	12.58 wt%
Magnesium	0.92 wt%
Aluminum	0.64 wt%
Silicon	2.28 wt%
Sulfur	22.49 wt%
Iron	3.27 wt%
Copper	56.92 wt%
Zirconium	0.91 wt%
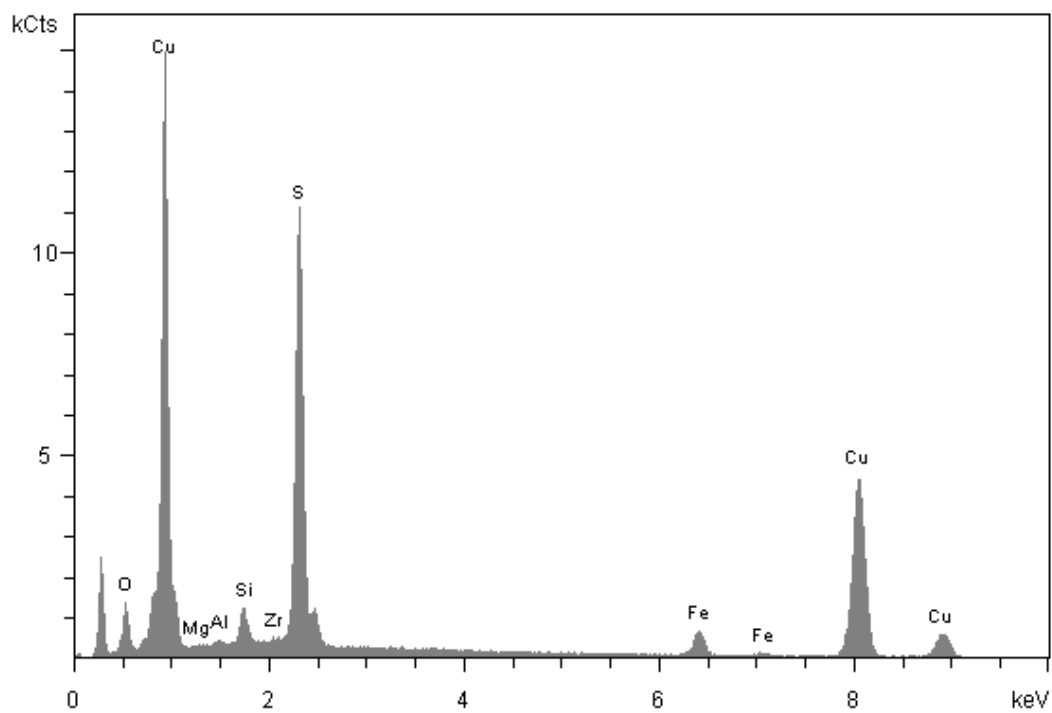
Figure A- 10: EDX analysis of "Enargite 1" sample after leaching during 1 hour in 2.5 M NaOH and 1.0 M Na₂S circled area 3.
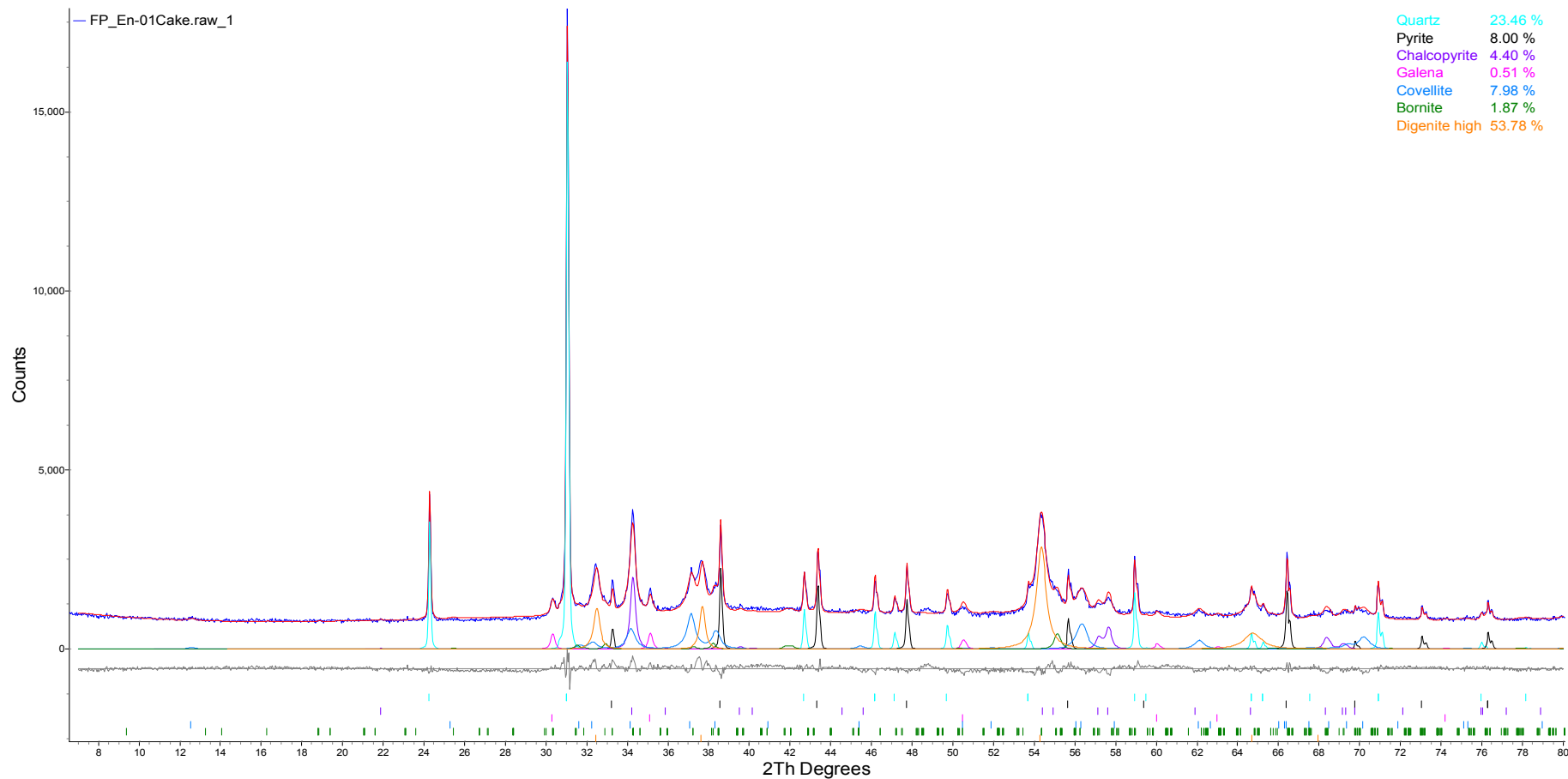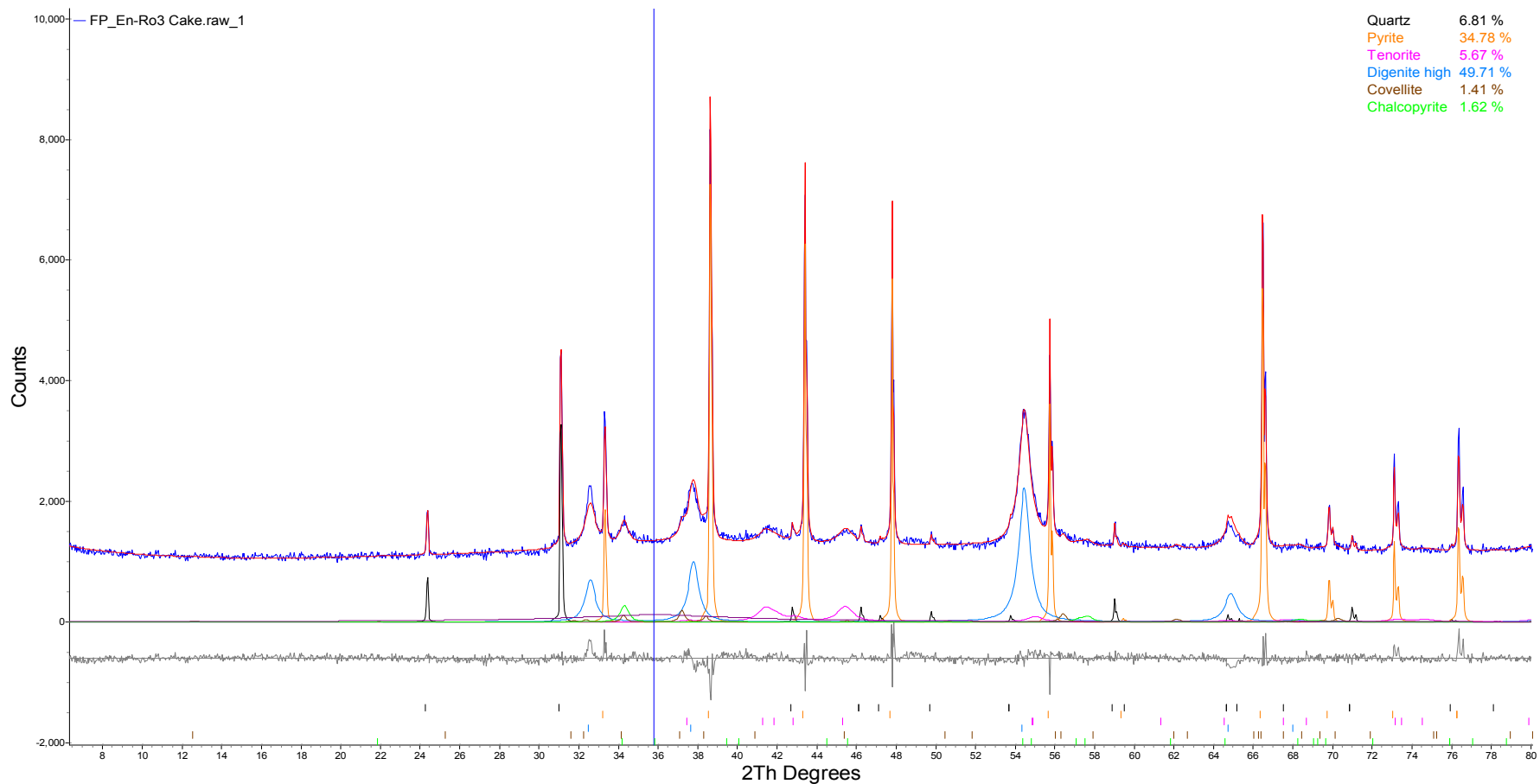
Figure A- 11: Rietveld refinement plot of "Enargite 1" sample after leaching during 1 hour in 2.5 M NaOH and 1.0 M Na$_2$S (blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases.
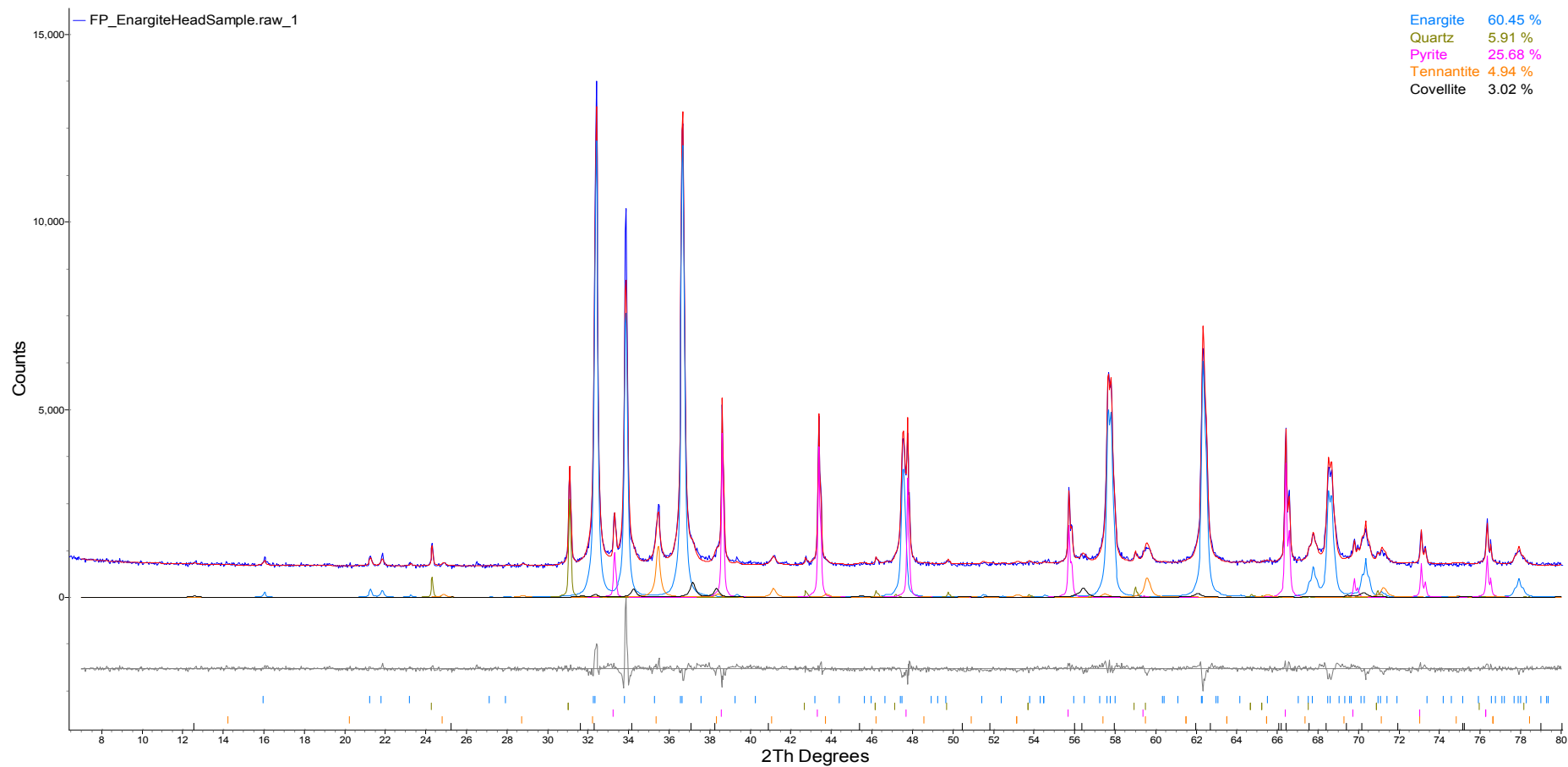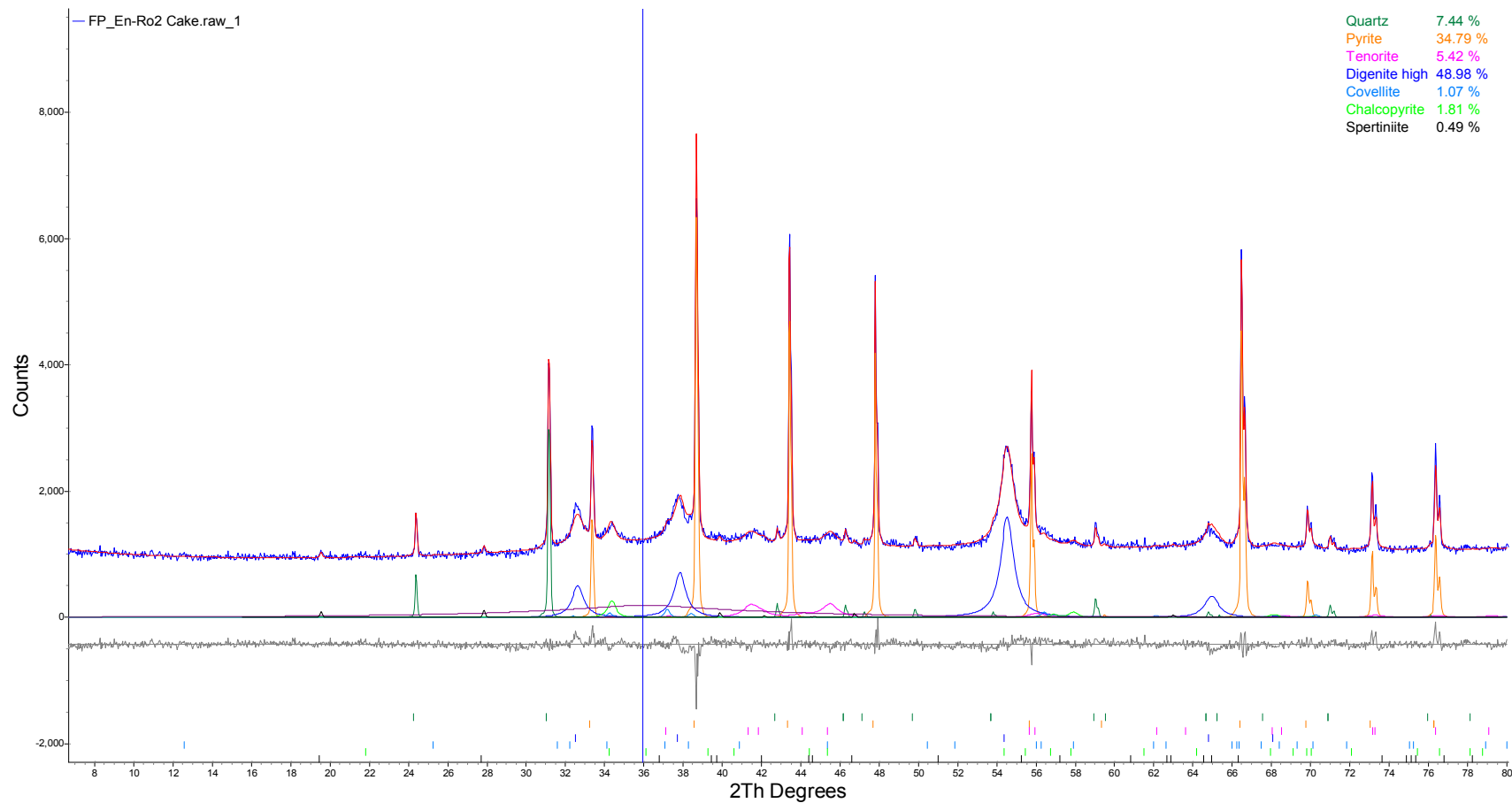
Figure A- 12: Rietveld refinement plot of sample "Enargite 2" head sample (blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases.
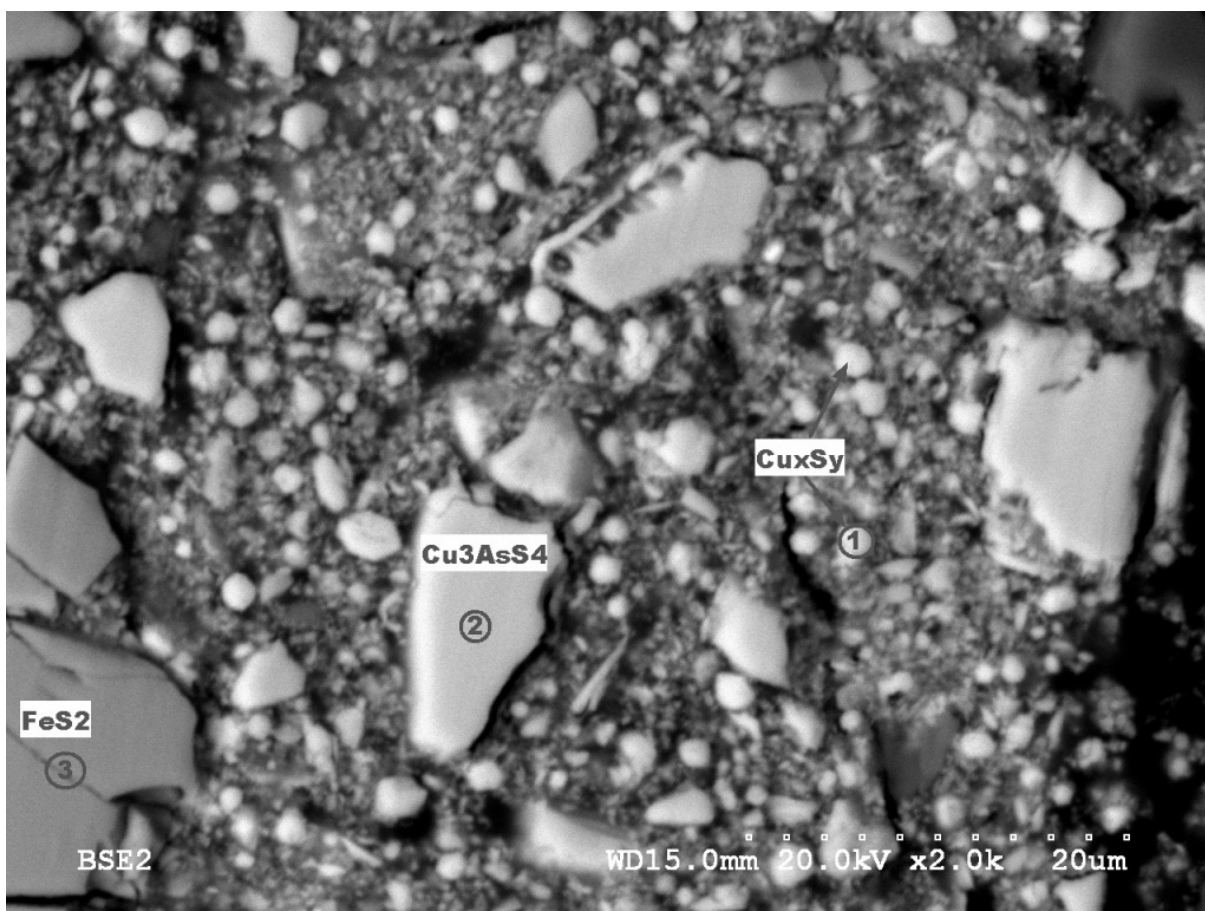
Figure A- 13: "Enargite 2" sample after leaching during 6 hour in 1.0 M NaOH and 0.5 M Na₂S.

Table A- 8: EDX analysis of "Enargite 2" sample after leaching during 6 hour in 1.0 M NaOH and 0.5 M Na₂S circled area 1.

Element	Concentration	
Silicon	1.75 at%	1.01 wt%
Sulfur	45.32 at%	29.91 wt%
Iron	4.10 at%	4.71 wt%
Copper	46.74 at%	61.14 wt%
Arsenic	2.09 at%	3.22 wt%

Figure A- 14: EDX analysis of "Enargite 2" sample after leaching during 6 hours in 1.0 M NaOH and 0.5 M Na₂S circled area 1.

Table A- 9: EDX analysis of "Enargite 2" sample after leaching during 6 hour in 1.0 M NaOH and 0.5 M Na₂S circled area 2.

Element	Concentration	
Silicon	1.13 at%	0.65 wt%
Sulfur	50.31 at%	33.21 wt%
Iron	1.18 at%	1.36 wt%
Copper	36.48 at%	47.74 wt%
Arsenic	10.66 at%	16.45 wt%
Antimony	0.24 at%	0.59 wt%

Figure A- 15: EDX analysis of "Enargite 2" sample after leaching during 6 hours in 1.0 M NaOH and 0.5 M Na₂S circled area 2.

Table A- 10: EDX analysis of "Enargite 2" sample after leaching during 6 hours in 1.0 M NaOH and 0.5 M Na₂S circled area 3.

Element	Concentration	
Carbon	68.13 at%	38.67 wt%
Silicon	0.20 at%	0.26 wt%
Sulfur	20.45 at%	30.98 wt%
Iron	9.93 at%	26.21 wt%
Copper	1.29 at%	3.88 wt%
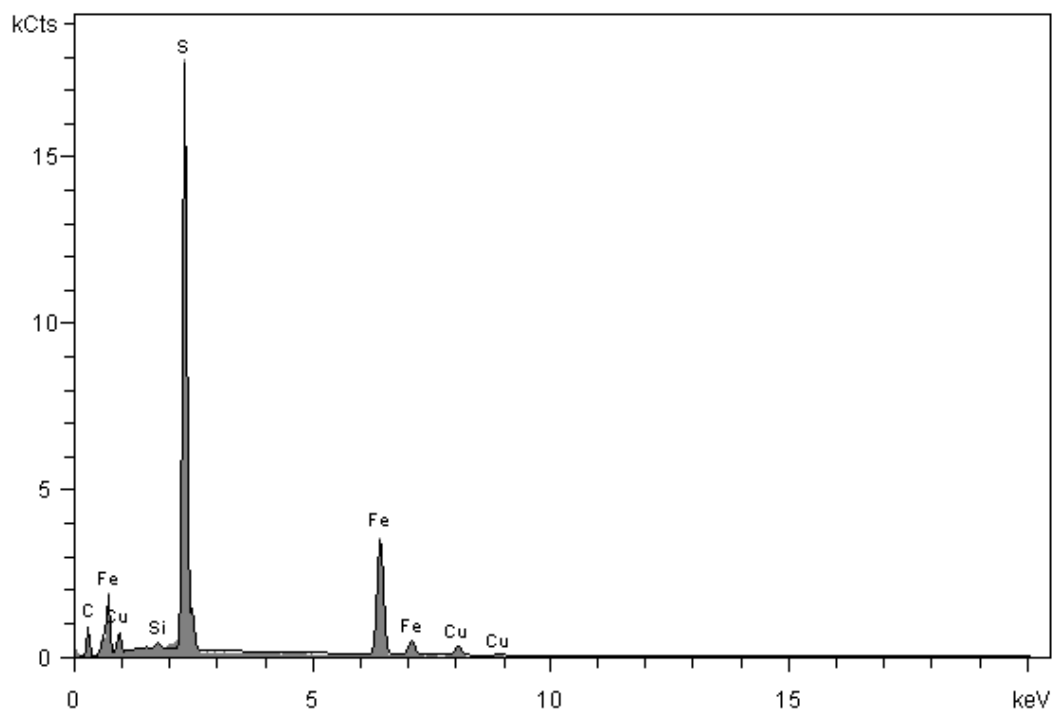
Figure A- 16: EDX analysis of "Enargite 2" sample after leaching during 6 hours in 1.0 M NaOH and 0.5 M Na₂S circled area 3.
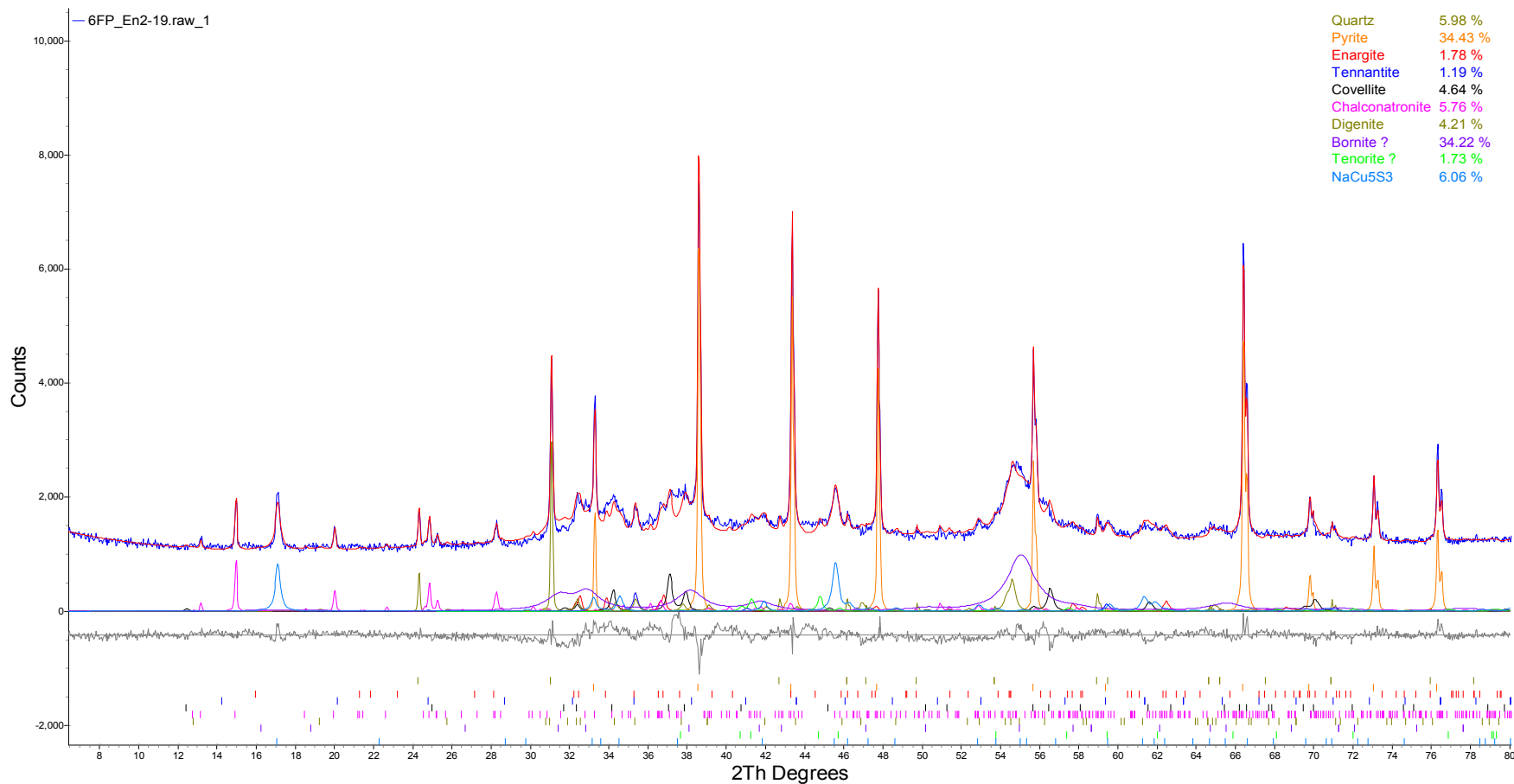
Figure A- 17: Rietveld refinement plot of sample "Enargite 2" sample after leaching during 6 hour in 1.0 M NaOH and 1.0 M Na₂S (blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases.
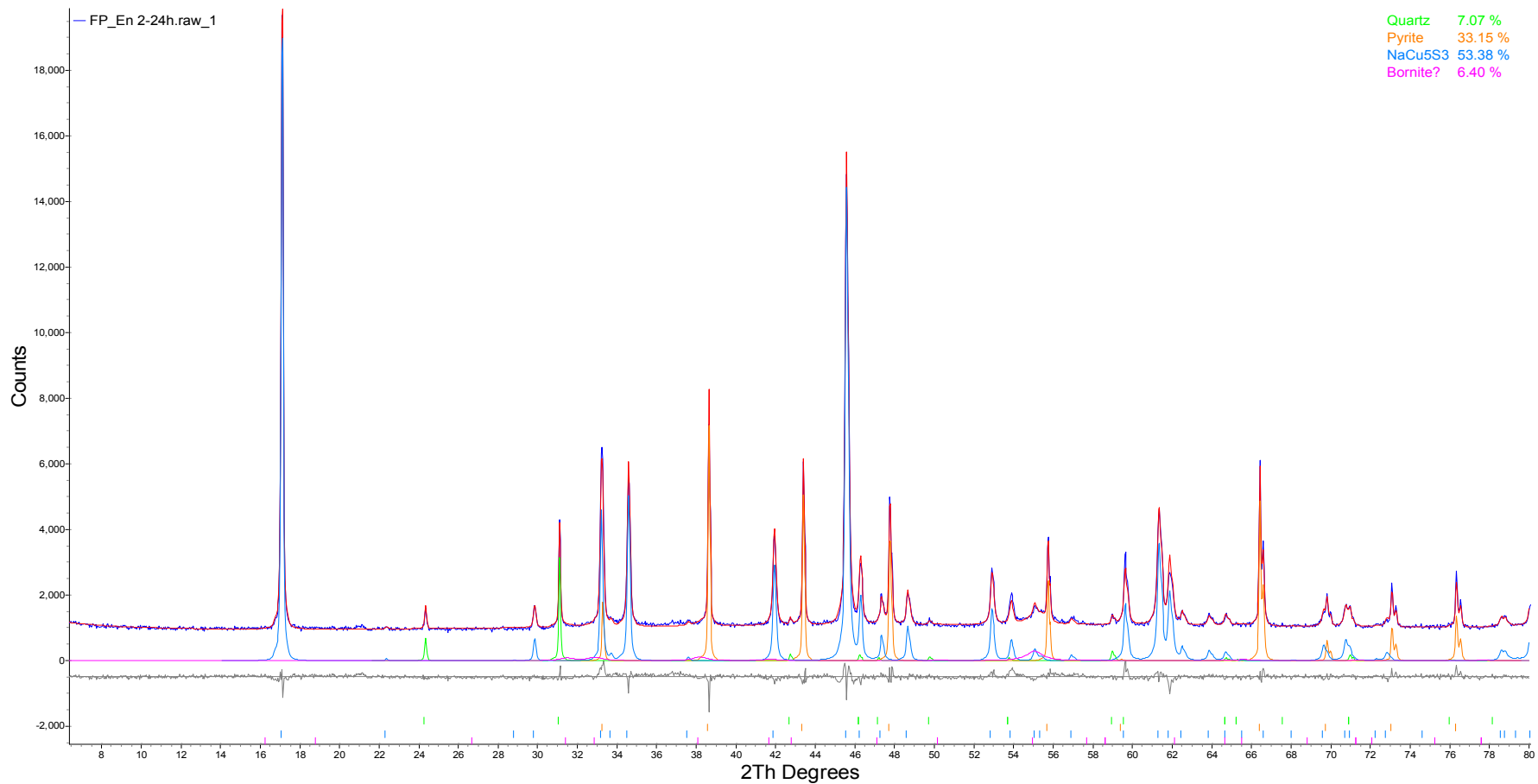
Figure A- 18: Rietveld refinement plot of "Enargite 2" sample after leaching during 24 hours in 2.5 M NaOH and 1.0 M Na₂S (blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases.
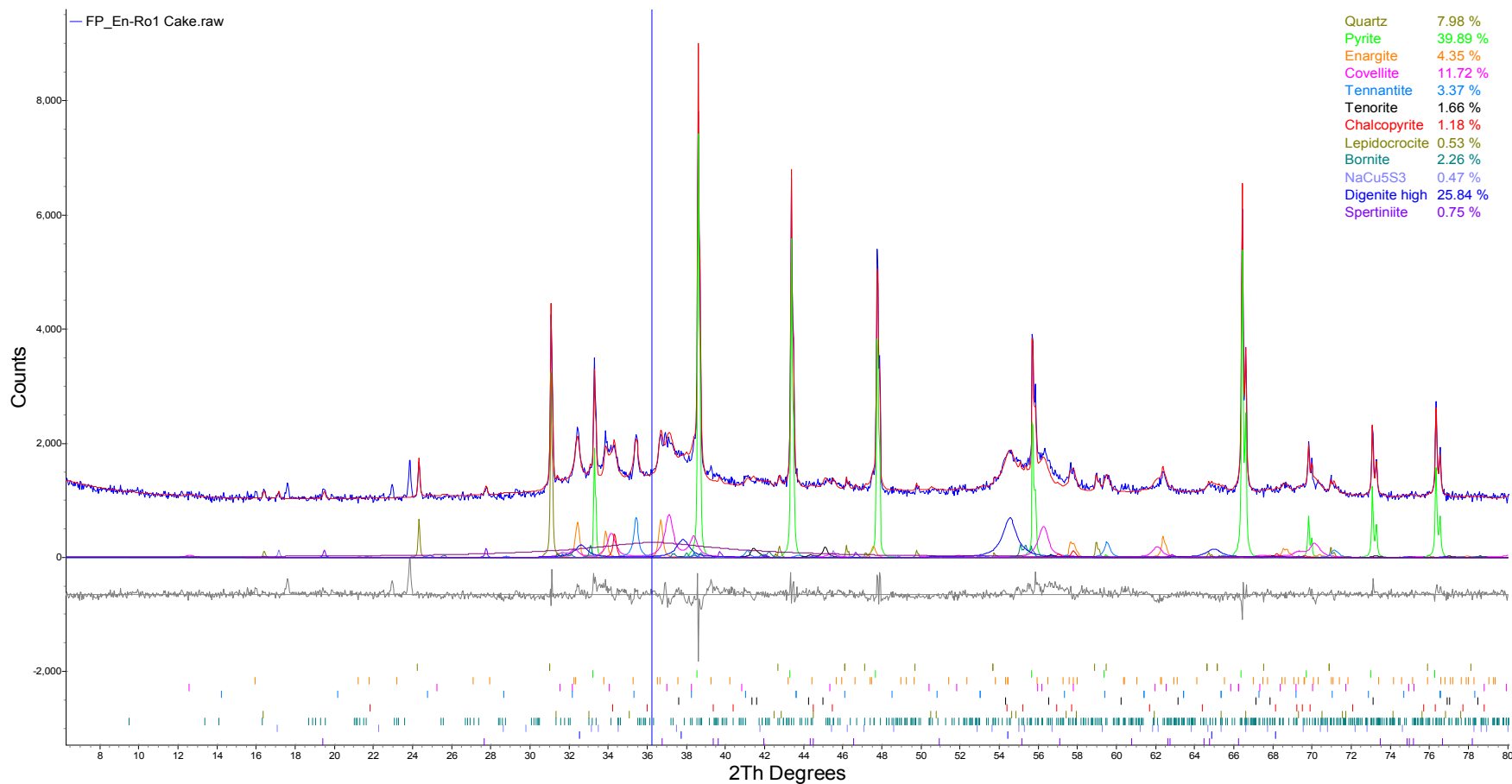
Figure A- 19: Rietveld refinement plot of "Enargite 2" sample after leaching during 2 hours 200 ml of solution containing approximately 100 % of the required stoichiometric reagents (blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases.

Figure A- 20: Rietveld refinement plot of "Enargite 2" sample after leaching during 2 hours 200 ml of solution containing approximately 150 % of the required stoichiometric reagents (blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases.

Figure A- 21: Rietveld refinement plot of "Enargite 2" sample after leaching during 2 hours 200 ml of solution containing approximately 200 % of the required stoichiometric reagents (blue line - observed intensity at each step; red line - calculated pattern; solid grey line below – difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases.

Appendix B

Arsenic precipitation using acidification, SEM micrographs, EDX and XRD analyses and spectra.
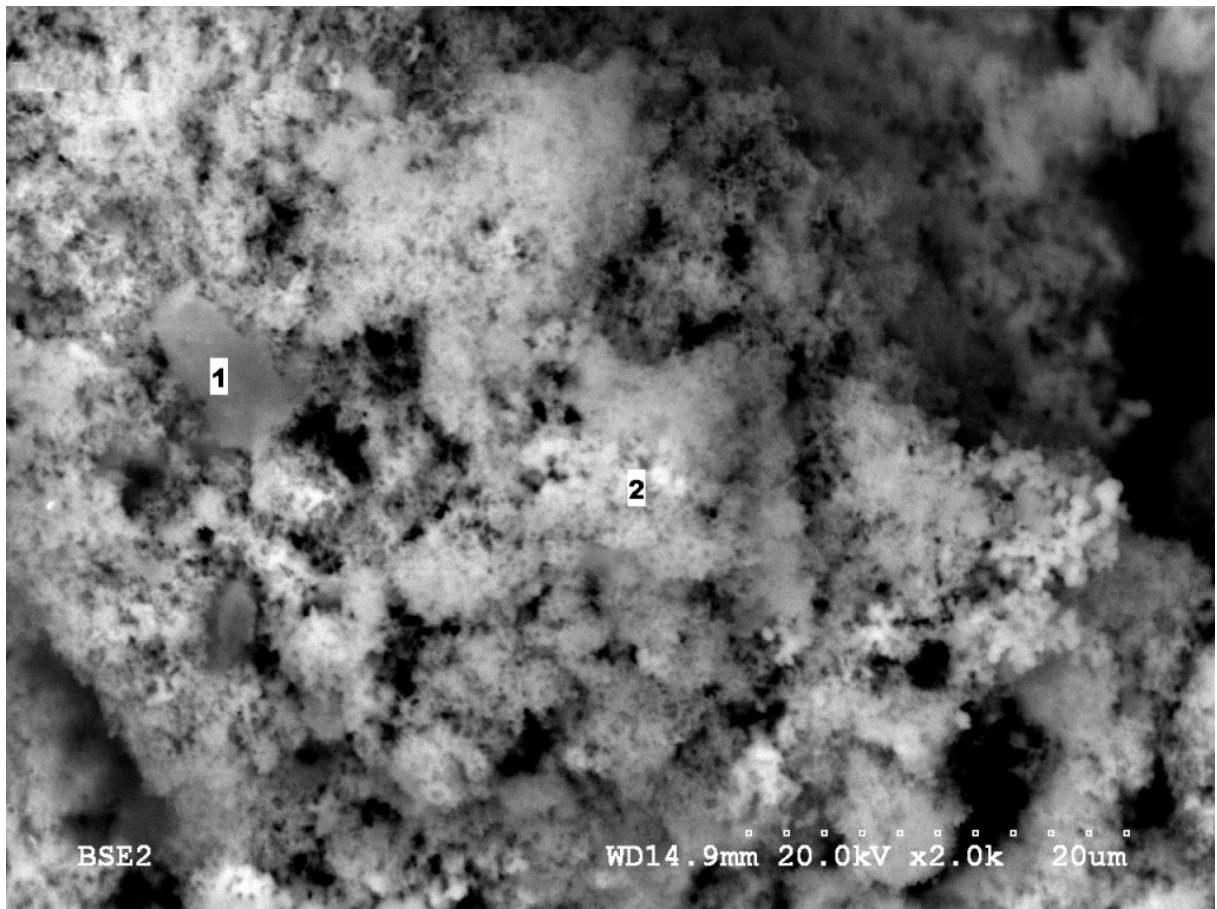
Figure B- 1: Arsenic precipitate micrograph after pH adjustment to a value of 2

Table B- 1: EDX analysis of arsenic precipitate after pH adjustment to a value of 2, area 1.

Element	Concentration	
Oxygen	42.84 at%	21.25 wt%
Sodium	3.77 at%	2.68 wt%
Silicon	5.26 at%	4.58 wt%
Sulfur	30.45 at%	30.27 wt%
Arsenic	17.59 at%	40.85 wt%
Antimony	0.10 at%	0.37 wt%
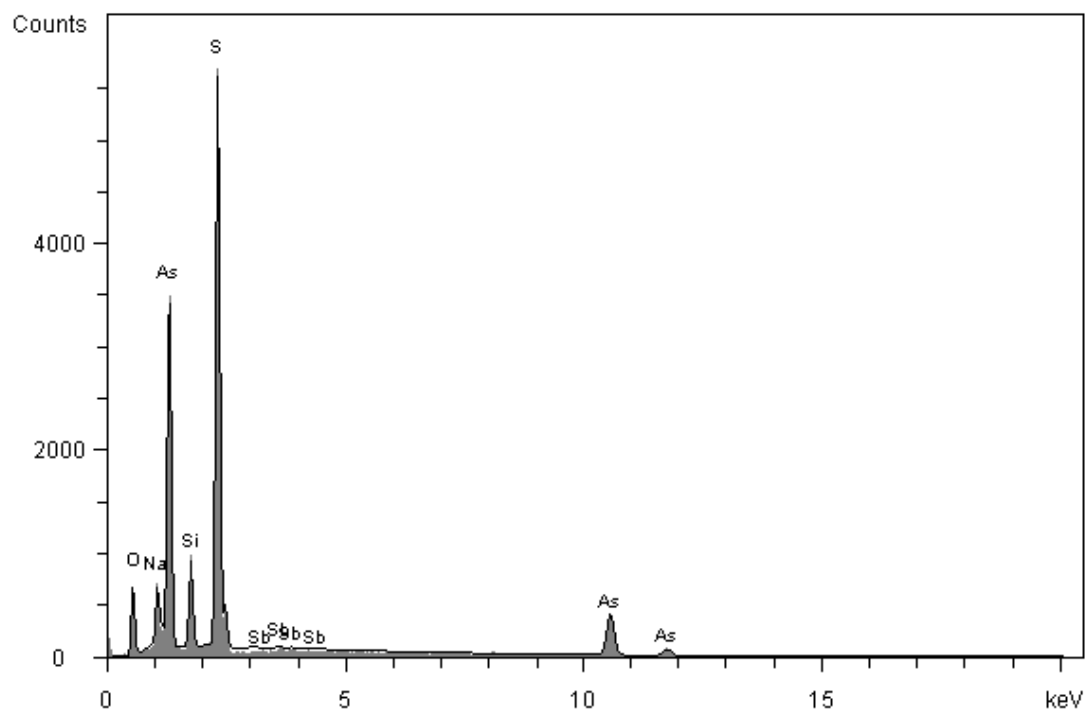
Figure B- 2: EDX analysis of arsenic precipitate after pH adjustment to a value of 2, area 1.

Table B- 2: EDX analysis of arsenic precipitate after pH adjustment to a value of 2, area 2.

Element	Concentration	
Oxygen	24.72 at%	10.68 wt%
Sodium	3.73 at%	2.31 wt%
Silicon	0.75 at%	0.57 wt%
Sulfur	49.56 at%	42.91 wt%
Arsenic	20.83 at%	42.16 wt%
Antimony	0.42 at%	1.37 wt%
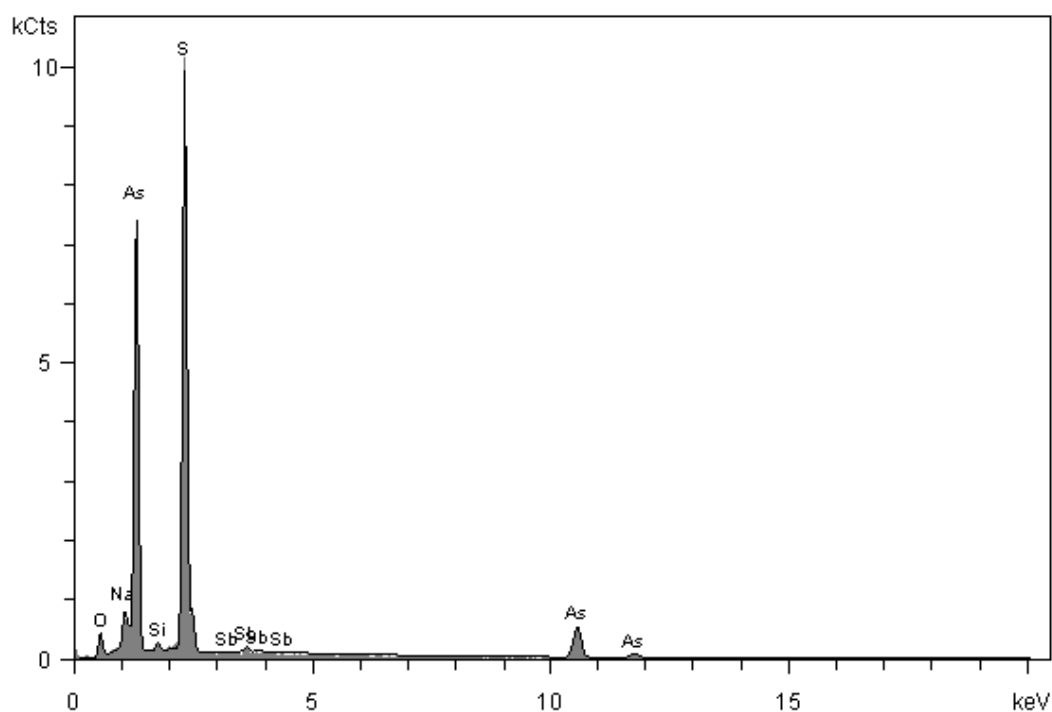
Figure B- 3: EDX analysis of arsenic precipitate after pH adjustment to a value of 2, area 2.
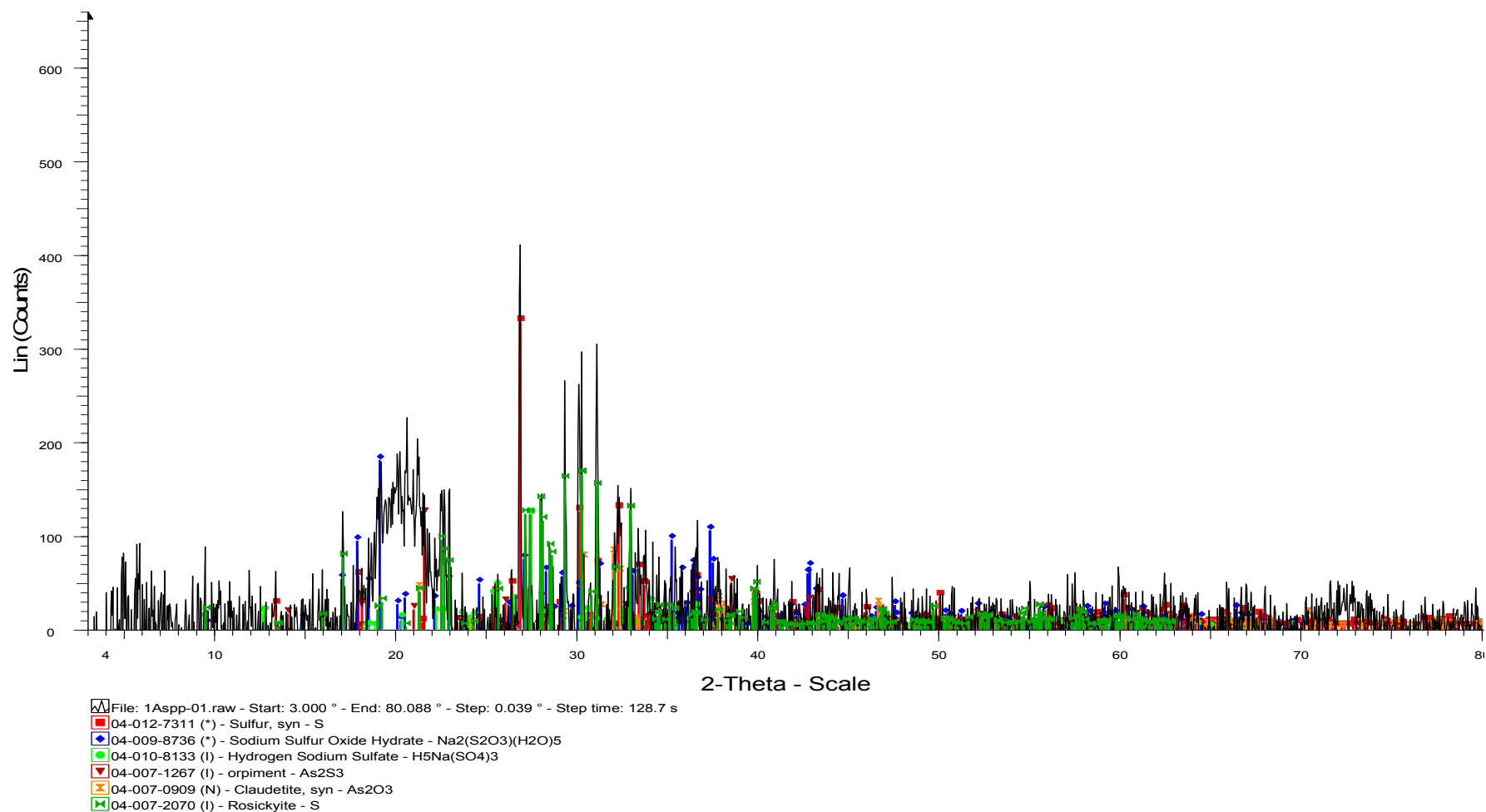
Figure B- 4: X-ray diffractogram of of arsenic precipitate after pH adjustment to a value of 3 – (Background subtracted).

Appendix C

XRD spectra of sodium-arsenate-sulphide compounds precipitated from enargite leach solutions under different conditions.
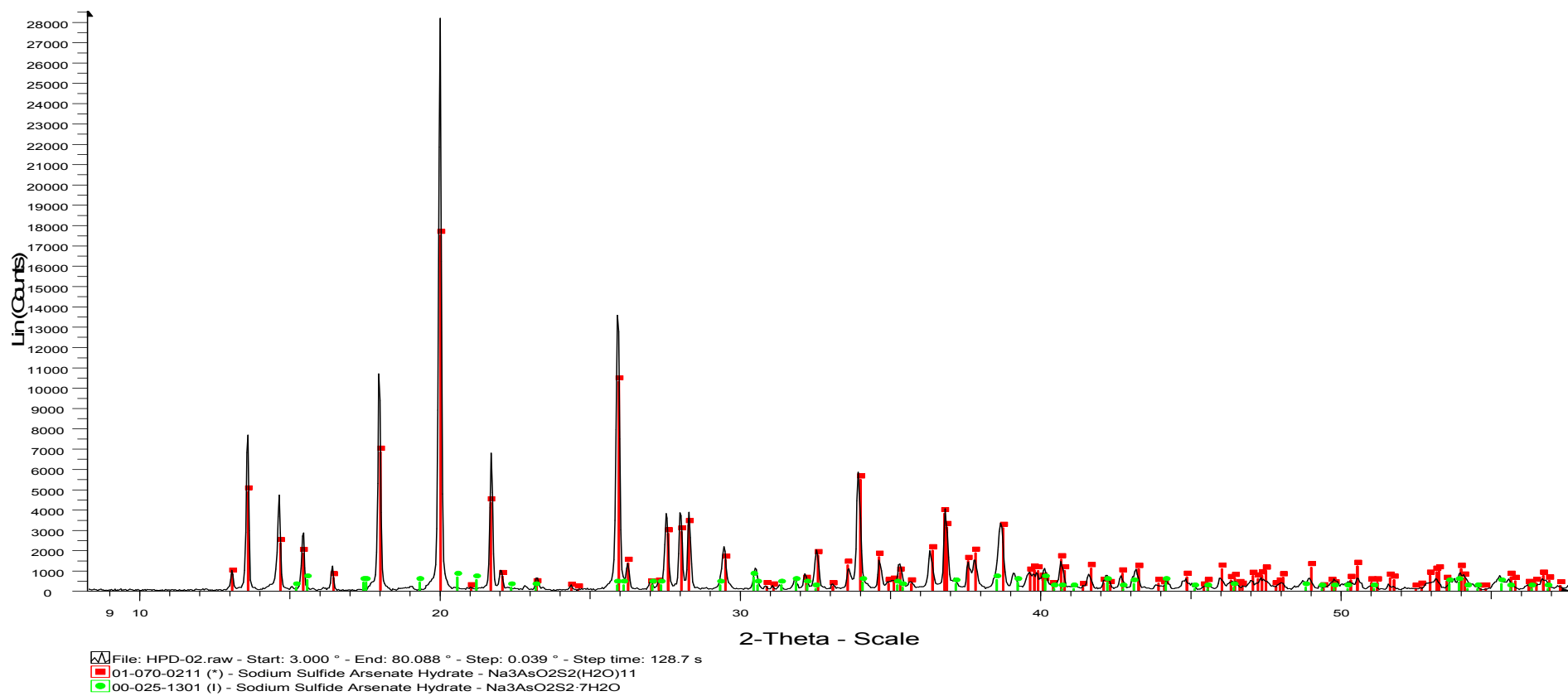
Figure C- 1: X-ray diffractogram of a sodium-arsenate-sulphide compound precipitated from enargite leach solution. Initial conditions include 200 grams of "Enargite 2" sample in 200 ml of a 2.5 M NaOH and 1.0 M Na₂S solution (Background subtracted).
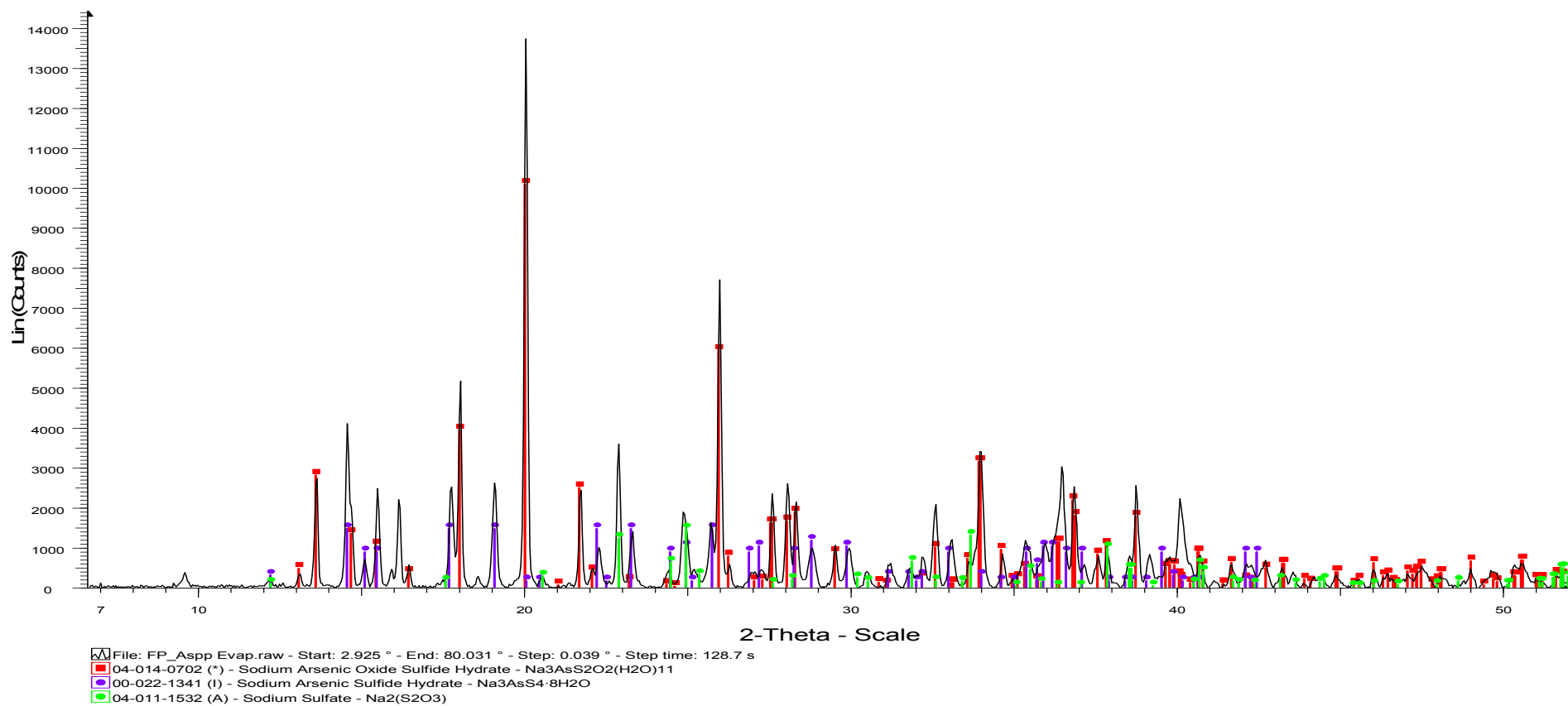
Figure C- 2: X-ray diffractogram of a sodium-arsenate-sulphide compound precipitated from enargite leach solution under the same conditions as Figure C-2, however, solid sample was not filtered, it was left at room temperature for one week to evaporate the water.
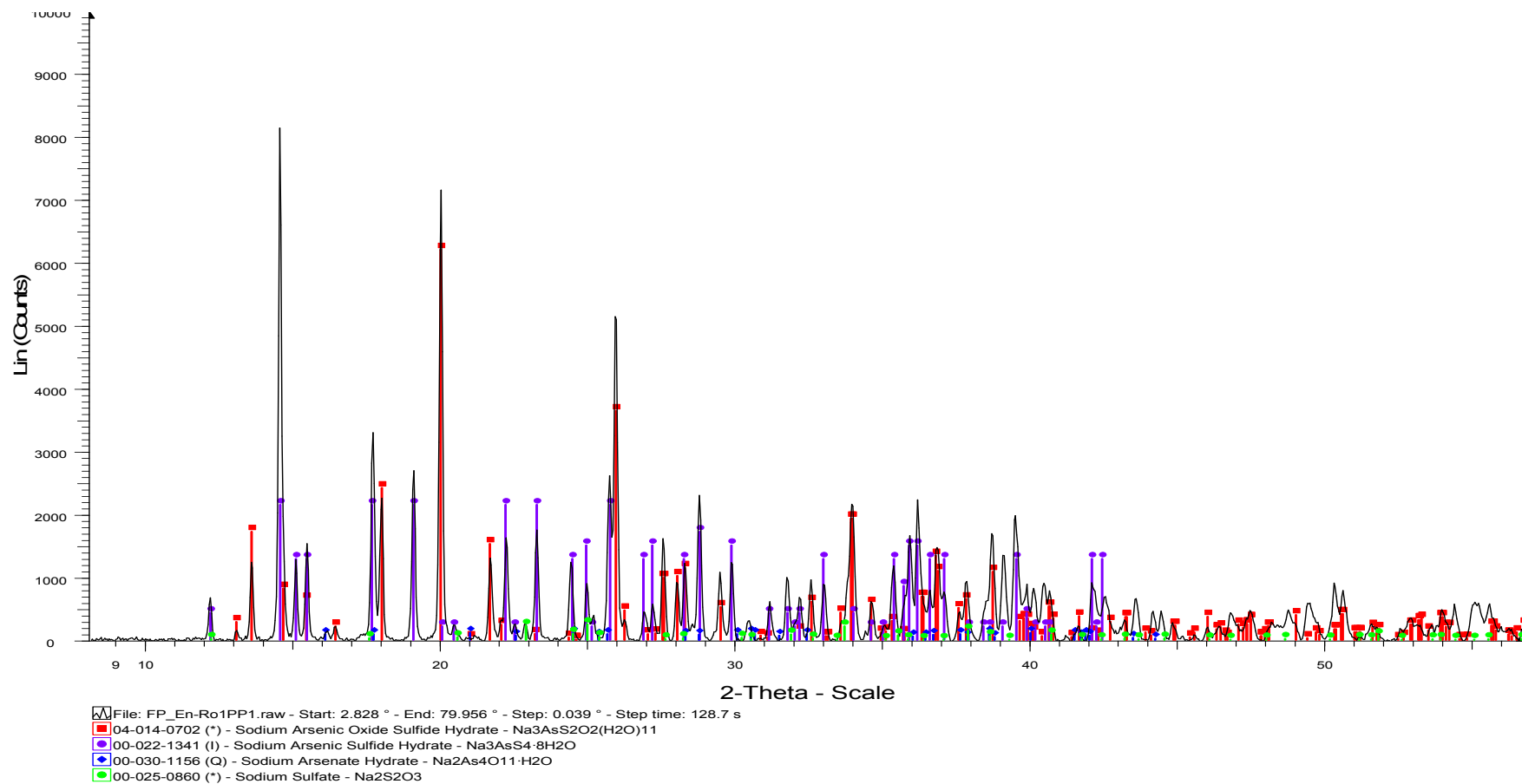
Figure C- 3: X-ray diffractogram of a sodium-arsenate-sulphide compound precipitated from enargite leach solution. Initial conditions include 200 grams of "Enargite 2" sample in 200 ml of a solution containing approximately 100 % of the required stoichiometric reagents.

Appendix D

Particle size distribution of "Enargite 2" head sample and enargite leach residues and effect of reagent concentration on As and Sb removal with error bars (+- 5 %).

Figure D- 1: Particle size distribution analysis of a leached "Enargite 2" sample residue after 24 hours in a 2.5 M NaOH, 1.0 M Na$_2$S solution at 95°C and 500 RPM.
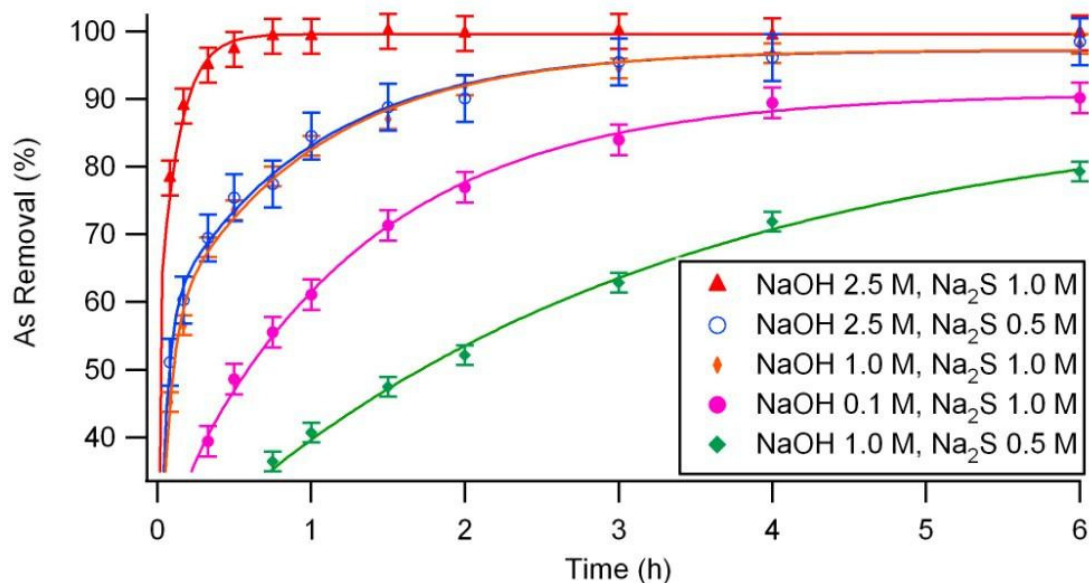
Figure D- 2: Effect of NaOH and Na₂S on As extraction at 95ºC using 10 g of enargite sample with a P₈₀ of 30 μm in 200 ml of solution and 500 RPM.

Figure D- 3: Effect of NaOH and Na₂S on Sb extraction at 95ºC using 10 g of enargite sample with a P₈₀ of 30 μm in 200 ml of solution and 500 RPM.

Table D- 1: Average standard deviation for the effect of NaOH and Na$_2$S on As and Sb extraction at 95°C using 10 g of enargite sample with a P$_{80}$ of 30 μm in 200 ml of solution and 500 RPM.

NaOH (M)	Na$_2$S (M)	Std. Deviation	
		As	Sb
2.5	1.0	2.54	1.35
2.5	0.5	3.44	4.19
1.0	1.0	1.48	2.06
0.1	1.0	2.25	2.75
1.0	0.5	1.44	0.84