Spectroelectrochemistry and modeling of enargite (Cu₃AsS₄) under atmospheric conditions

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SPECTROELECTROCHEMISTRY AND MODELING OF ENARGITE (Cu$_3$AsS$_4$)
REACTIVITY UNDER ATMOSPHERIC CONDITIONS

By

Robert Nicholas Verne Gow

B.S. Metallurgical and Materials Engineering, Montana Tech of the University of Montana, Butte, MT, 2008
M.S. Metallurgical Engineering, Montana Tech of the University of Montana, Butte, MT, 2008

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Approved by:

Courtney Young, Co-Chair
Metallurgical and Materials Engineering - Montana Tech

Edward Rosenberg, Co-Chair
Chemistry – The University of Montana

Sandy Ross, Dean of The Graduate School
Graduate School - The University of Montana

Jerome Downey
Metallurgical and Materials Engineering - Montana Tech

Hsin Huang
Metallurgical and Materials Engineering - Montana Tech
Spectroelectrochemistry and Modeling of Enargite (Cu$_3$AsS$_4$) Reactivity under Atmospheric Conditions

Co-Chair: Courtney Young - Montana Tech of the University of Montana
Co-Chair: Edward Rosenberg - The University of Montana

Raman spectroscopy has been a useful technology for fundamental studies in the mining industry. Surface changes through oxidation and reduction reactions can be monitored in-situ, allowing the changes to be monitored in real time. In conjunction with cyclic voltammetry, to change the conditions at which a mineral surface is subjected to, reaction and reaction conditions can be identified. The results can then be plotted to create a map similar to that of an E$_H$-pH diagram.

In this study, the copper arsenic sulfide mineral, enargite (Cu$_3$AsS$_4$) was subjected to a series of tests. Relatively pure samples were obtained from Butte, MT and Quirivilca, Peru and used to create mineral electrodes. The electrodes were cycled over an E$_H$ range of -1000 to +1000 mV (vs SHE) at pH values ranging from 1 to 13. Changes to the surface of the mineral were identified by comparing Raman spectra to a mineral Raman database. Plotted results were then compared against mass-balanced E$_H$-pH diagrams for the Cu-As-S-H$_2$O system, created using the STABCAL thermodynamic calculation program. Ultimately, the E$_H$-pH diagram is modified based on the results, and an updated version was created.

The mass-balanced methodology is applied, in conjunction with Gibbs’ phase rule, to an aqueous quaternary system. Variations in E$_H$-pH diagrams of the Cu-As-S-H$_2$O system based on slight changes in concentrations of copper, arsenic and sulfur are examined.

Finally, a novel nano-graphene material was tested for its ability to adsorb arsenic. Arsenic remediation, downstream of an enargite leach, remains an unsolved issue. The nano-graphene platelets were not able to successfully reduce arsenic levels in solution below the EPA-required limitation of 10 ppb. A thermodynamic evaluation of the adsorption characterized the process as physisorption, and likely unsuitable for long-term arsenic storage. A functionalized version of the nano-graphene may enhance results.
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1. Proposed Work and Objectives

The copper mineral enargite, Cu$_3$AsS$_4$, was identified as a particular mineral of interest to the Newmont Mining Company due to its refractory nature and the environmental hazards associated with processing of arsenic-bearing minerals. In the gold processing flowsheet, both copper and arsenic are problematic, as copper consumes large amounts of cyanide and arsenic will consume oxygen, both of which are necessary for cyanide dissolution of gold via the Elsner equation:

$$4 \text{Au} + 8 \text{NaCN} + \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 4 \text{Na[Au(CN)]}_2 + 4 \text{NaOH}$$

Arsenic-bearing minerals must then be removed and are typically concentrated into what is termed a “dirty” con. There are few current methods employed to deal with such a concentrate. Therefore, it was determined that a thermodynamic evaluation of the copper-arsenic-sulfur-water system would help to fill a void in literature knowledge and determine possible avenues of hydrometallurgical processing. After meeting with representatives from the Newmont Mining Corporation, the following tasks were established:

**Task 1** Compile a thermodynamic database for Cu-As-S system

- Comparison of Cu-As-S Mass Balanced and Line Plot Diagrams *(Chapter 6)*
- Comparison of plots Oxidation to Sulfate vs Oxidation to Elemental Sulfur at Varying Cu:As:S Ratios *(Chapter 7)*

**Task 2** Modification and Validation of Thermodynamic Models using a combination of Raman Spectroscopy and Cyclic Voltammetry

- Reactivity in Alkaline Solutions (Selective As Leach) *(Chapter 3)*
- Reactivity in Acidic Solutions (Co-dissolution of As and Cu) *(Chapter 4)*
- Addition of HS⁻ as a lixiviant (Chapter 5)

**Task 3** Determine Viability of Arsenic Adsorption using a Nanographene Material

- Novel nano-graphene material as an arsenic adsorbent (Appendix D)

The initial objective of Task 1 was to search for and compile all possible speciation data for the copper-arsenic-sulfur-water system. Line plot $E_H$-$pH$ diagrams were plotted and then compared against diagrams calculated using the mass-balanced method. Differences in the diagrams were expected due to the errors associated with using the line-plot methodology in a quaternary system.

Two separate enargite crystals were obtained for the surface reaction testing in Task 2. The first piece was a single enargite crystal from the Leonhard Mine in Butte, MT and the second was from the Quirivilca region in Peru, obtained from Mineral Zone in Tucson, Az. Surface reactions of the minerals, as they were subjected to changing solution conditions, were recorded by cyclic voltammetry and identified via Raman Spectroscopy.

Finally, arsenic remediation was identified as an issue that arises from processing of enargite and other arsenic-bearing sulfides. The current EPA Best Developed Available Technology is adsorption of arsenic by ferrihydrite, which can be costly. A nano-graphene adsorbent material was chosen as a potential replacement technology. Compared to single or multi-walled carbon nanotubes, nano-graphene platelets, provided by Petrov-nGP, have a much higher surface area, potentially providing higher adsorption capabilities. This work was conducted by two undergraduate students, for the Undergraduate Research Program at Montana Tech, under the guidance of this project.

All of these results will be discussed within this report. Each of the three tasks is broken into appropriate subcategories, which will serve as the chapters. Each chapter was written as a
publication to be submitted to the appropriate journals. The mineral characterization results and the raw cyclic voltammograms are included in the Appendices.
2. Literature Review

2.1 Enargite Properties

The review for the work compiled here will briefly summarize current literature, as not to rewrite previous comprehensive reviews, and various aspects of other studies. The thermodynamic properties have been less frequently examined, and as such, it will be necessary to compile and then expand on the thermodynamic aspects of enargite and other copper-arsenic minerals within literature.

The most commonly referred of these copper-arsenic minerals are enargite (Cu$_3$AsS$_4$) and tennantite(Cu$_{12}$As$_4$S$_{13}$); although, several other species have been noted in literature, such as sinnerite(Cu$_6$As$_4$S$_9$), lautite(CuAsS), and enargite’s polymorph, luzonite (Cu$_3$AsS$_4$).

Enargite is a copper arsenic sulfide, which has also been termed a copper-arsenic sulfosalt, as explained by Craig and Barton (1973), or cuprous thioarsenate (Secco at al., 1988). It is commonly associated with pyrite and other copper and arsenic sulfides, such as chalcopyrite, chalcocite, covellite, digenite, tennantite, sphalerite and galena (Lattanzi et al., 2008). There are only a few locales that have reported large bodies of copper-arsenic mineralization. Enargite and tennantite have been found within the U.S.; at the Leonhard Mine in MT, the Tintic district of Utah and in the Red Mountain District of Colorado. They have also been indicated in Quirivilca, Peru and the La Rioja Province of Argentina. Other instances have been noted at specific mines in Taiwan, Japan, Italy and Namibia (Fang et al., 2004; Anthony et al., 2005; Fantauzzi et al., 2007).

It is also common to find enargite substituted with up to 6 wt% antimony (Springer, 1969), and associated with other minerals belonging to the corresponding Cu-Sb-S series: tetrahedrite and famatinite. The structure of enargite is orthorhombic, similar to that of wurtzite.
(ZnS), as seen in Figure 1. The zinc positions are replaced by monovalent copper and pentavalent arsenic atoms.

Figure 2-1. Enargite Structure (Adapted from Parthe, 1964).

Enargite is considered to be one of the most refractory copper sulfides as is seen in the following series of reactivity in ammonia solutions (Kuhn et al. (1974):

Chalcocite > Covellite > Bornite > Chalcopyrite > Enargite

and in ferric sulfate solutions (Sullivan, 1933).

Bornite > Covellite > Chalcocite > Chalcopyrite > Enargite

In either instance, the reactivity of enargite is considered to progress extremely slowly. At approximately 48% by weight copper, enargite is slightly lower in copper content compared to primary copper sulfides, chalcocite (80%) and covellite (66%), but still a significant source of
compared to other copper-bearing sulfides. As such, its processing has been widely studied in an effort to find a suitable and economical method that also solved the issue of how to treat the arsenic waste afterwards.

A review of arsenic remediation technology was compiled by Twidwell and McCloskey (2011). The U.S. Environmental Protection Agency has identified arsenic adsorption by ferrihydrite as the Best Developed Available Technology (BDAT); although, research continues to find a process that is comparatively more suitable for long-term storage of arsenic, and is more economically competitive.

2.2 Previous Literature Reviews

Two comprehensive literature reviews (Lattanzi et al., 2008; Safarzadeh et al., 2014) have recently been published which focus on the processing of enargite-bearing ores.

Lattanzi et al. (2008) focused on the oxidative reactions of enargite in both “natural and quasi-natural (mining) situations,” compiling information on enargite characteristics, natural weathering of the enargite surface, and forty individual academic studies. The authors determined that the oxidation of enargite in solution at low pH is relatively slow compared to the oxidation rate at higher pH. Oxidation in acidic solutions would require solutions potentials greater than 0.5 V vs SHE, similar to oxidative leaching of chalcopyrite. At potentials this high, it is common to form elemental sulfur on the surface as the mineral becomes depleted of copper and arsenic. They also note that many of lab-scale tests are conducted on polished surfaces of enargite, which may not be representative of an untreated surface.

Safarzadeh et al. (2014) compiled information more relevant to the methods that have been utilized for the processing of enargite-bearing concentrates; lab-scale and industrially applied. There are two main process methodologies that have been investigated for application to
arsenic-bearing concentrates. The most commonly referred to can be characterized as either a highly oxidative leach under acidic conditions, such as in Galvanox (Dixon et al., 2008) or CESL (Deffreyne and Cabral, 2009; Mayhew et al., 2010), or a selective leach under alkaline conditions to leave behind an arsenic-free concentrate, using sodium hypochlorite (Mihajlovic, et al., 2007) or sodium sulfide, as in the alkaline sulfide leach (Anderson and Twidwell, 2008a, b).

Bio-leaching options such as the BacTech/Mintek (Wang, 2005; Habashi, 2009) and GEOCOAT (Bath et al., 2005; Ford et al., 2009) processes have also been implemented at a pilot-scale but were never fully implemented due to slow leach rates. As bio-leaching was not a task covered within the current study, these processes will not be discussed further.

2.2.1 Acidic Leaching

In low pH systems, the pH is typically at or below 1. Under atmospheric pressure, and temperatures upwards of 100°C, the leaching of enargite was slow, approximately 6% arsenic in 7 hours (Padilla et al., 2005). As the mineral surface was depleted of copper and arsenic, the formation of an elemental sulfur coating would prevent the leaching process from going to completion:

\[
2\text{Cu}_3\text{AsS}_4 (s) + 6\text{H}_2\text{SO}_4 (aq) + 5.5\text{O}_2 (aq) \rightarrow 6\text{CuSO}_4 (aq) + 2\text{H}_3\text{AsO}_4 (aq) + 8\text{S}^0 + 3\text{H}_2\text{O}
\]

Further studies (Riveros and Dutrizac, 2008) found that by increasing the leaching temperature above 170 °C, elemental sulfur production could be prevented by forcing sulfate formation instead. By increasing the temperature to 220 °C and the oxygen partial pressure to 689 kPa, the enargite could be completely dissolved in two hours (Padilla et al., 2008).

The CESL (Cominco Engineering Services Limited) process improves upon the slow kinetics by increasing the temperature up to 150°C and the addition of chloride to the leach, at concentrations up to 25 g L⁻¹. The chloride ions prevent passivation by elemental sulfur;
however, the process requires additional stages and specialized materials to handle the highly corrosive solution.

It is also possible to increase the reaction rate by blending pyrite or chalcopyrite into the concentrate. The ferric ions create a galvanic interaction which allows for the leaching process to occur under atmospheric conditions (Dixon et al., 2008). This process, known as Galvonox, has been patented by the University of British Columbia, and is being evaluated for success at pilot scale.

2.2.2 Alkaline Leaching

Under alkaline conditions, it is possible to selectively leach arsenic, leaving copper either as CuO or CuS. In a proposed method (Mihajlovic, et al., 2007), sodium hypochlorite is used to covert enargite to CuO and AsO$_4^{3-}$:

$$2Cu_3AsS_4(s) + 35NaClO(aq) + 22NaOH(aq) \rightarrow$$

$$6CuO(s) + 2Na_3AsO_4(aq) + 8Na_2SO_4(aq) + 35NaCl(aq) + 11H_2O$$

At slightly elevated temperatures, approximately 60 °C, arsenic leaching was completed in two hours.

The processing of enargite has also been examined using an alkaline sulfide leach (Holmes and Coltrinari, 1973; Coltrinari, 1977; Anderson and Twidwell, 2008a,b):

$$2Cu_3AsS_4(s) + 3Na_2S(aq) \rightarrow 3Cu_2S(s) + 2Na_3AsS_4(aq)$$

This process was used for several years at the Sunshine Mine (Anderson et al., 1991) and the Equity Silver Mine (Dayton, 1982). The reaction is enhanced by increasing the concentration of Na$_2$S and NaOH. Sodium hydrosulfide, NaSH, may be preferred to Na$_2$S since it has a higher weight percent of sulfide. Under the proposed reaction, it was found that arsenic could be completely reacted within a few hours (Curreli et al., 2009; Tongamp et al., 2010a). Solubilized
arsenic can then be crystallized out as a sodium salt for further treatment. (Tongamp et al., 2010b)

2.2.3 Pretreatment Options

More recent studies have attempted various pretreatment options to render enargite more amenable to leaching. A series of papers (Achimovicova et al., 1999; Balaz et al., 2000; Balaz and Achimovicova, 2006), examined the ability of “mechanical activation” to improve upon the kinetics of the alkaline leach process. By increasing the surface area of an enargite concentrate from 1.3 m$^2$ g$^{-1}$ to 18.1 m$^2$ g$^{-1}$ by fine grinding in a stirred ball mill, the authors were able to reduce the time necessary to leach arsenic from 120 min to 3 min. They also increased the amount of arsenic leached from 86% to 98%.

Hol et al. (2012) investigated bio-based pretreatment options to break through the elemental sulfur layer that can plague refractory sulfide leaching. The authors target was to convert elemental sulfur to hydrogen sulfide to prevent surface passivation and increase extraction of gold associated with enargite. They were able to improve extraction from 49 to 70%.

Safarzadeh and Miller (2014) applied an acid-bake process, which had historically been used by the Anaconda Company to treat copper concentrates. The process mixes a concentrate with sulfuric acid at temperatures up to 200 °C in order to covert sulfide minerals to water-soluble sulfates. The process was eventually abandoned due to SO$_2$ emissions (Habashi, 2005). The authors were able to water-leach 87% of the Cu and 64% of the As after acid-baking an enargite-concentrate. Some of the arsenic was lost to the gas phase. However, the authors anticipate that the simplicity of the process may overcome the emissions issue.
2.3 Thermodynamics of Enargite

Craig and Barton (1973) published a paper on their method to approximate the free energy of formations of sulfide minerals which is the basis of all thermodynamic knowledge on copper-arsenic sulfides. The authors state that the free energy of formations can be roughly estimated based on the mixing of their simpler sulfide components. The values for enargite, tennantite and sinnerite are based on the following equations:

\[ \Delta G_{\text{Enargite}} (\text{kcal}) = -104458 + 56.16 \times T \]
\[ \Delta G_{\text{Tennantite}} (\text{kcal}) = -355468 + 172.28 \times T \]
\[ \Delta G_{\text{Sinnerite}} (\text{kcal}) = -104458 + 56.16 \times T \]

A previous publication (Craig and Lees, 1972) details the process behind these approximations. The free energies of reaction for the sulfosalts assume the standard state of sulfur to be the diatomic gas \( \text{S}_2 \), which must be converted to elemental sulfur, \( \text{S}^0 \), for use in \( E_H \)-pH calculations. The free energy of this conversion, using the value for sulfur gas from the NBS database (Wagman et al., 1982), is shown below:

\[ 4\text{S}^0 \rightarrow 2\text{S}_2(\text{g}) = 37.906 \text{ kcal} \]

The free energies of formation, at 25 °C (298.15K), used in all of the \( E_H \)-pH diagrams in this study are then as follows:

\[ \Delta G_{\text{Enargite}} = -49.808 \text{ (kcal/mol)} \]
\[ \Delta G_{\text{Tennantite}} = -110.256 \text{ (kcal/mol)} \]
\[ \Delta G_{\text{Sinnerite}} = -180.908 \text{ (kcal/mol)} \]

Other commonly cited sources of thermodynamic data for enargite are Knight (1977) and Seal et al. (1996). The standard enthalpy and entropy values of enargite are listed as -42.81 kcal/mol and 61.6 cal/mol respectively. However, these values are based on the thermodynamic
approximations of Craig and Barton (1973). Seal et al. (1996) determined the heat capacity of synthetic enargite samples to be $47.01 + 1.19 \times 10^{-2}T - 0.458 \times 10^{6}T^{-2}$ (cal/K·mol)

2.4 Thermodynamic Databases

To complete task 1, a thorough review of literature was conducted to compile all possible species of the copper-arsenic-sulfur-water system. The MINTEQ2A (Allison et al., 1991) database contained the majority of the free energy values that were used. The database was then supplemented with values from the US Geological Survey database (Robie, 1984) and other authors listed throughout Chapters 3-7 as they are used. For instances of duplicate values between sources, the MINTEQ2A database was used as the primary source.

The completed database, found in Appendix C, was used to generate several initial $E_{H}$-pH diagrams to compare against those previously published (Asbjornsson et al., 2003; Padilla et al., 2008). The initial mass-balanced diagram created for this study, Figure 2, was compared against the previous diagrams, Figures 3 and 4.

There are discrepancies between the species that appear in the three diagrams and the boundaries of regions common between them. Figure 2 includes regions for the other copper arsenic minerals, tennantite and sinnerite. Olivinite, a copper arsenate hydroxide and the soluble thioarsenate species ($\text{AsS}_{4}^{3-}$), which is key in the alkaline sulfide leach. The boundaries of the predominant species are likely different due to the mass-balanced method used to calculate the diagrams in this study. The mass-balanced method, more fully explained in Chapters 6 and 7, better accounts for the competing equilibria of the multiple components and provides a more accurate diagram for a four component system such as the Cu-Fe-S-H$_{2}$O system (Huang and Young, 1996). The Cu-As-S-H$_{2}$O system is fully explored in this study in Chapters 3-7.
Figure 2-2. Complete $E_\text{H}$-pH Diagram for the Cu-As-S system, $[\text{Cu}]=7.5\text{E}-2\text{M}$, $[\text{As}]=2.5\text{E}-2\text{M}$, $[S]=1.0\text{E}-1\text{M}$. Sulfur oxidation includes all sulfoxy species.
Figure 2-3. Metastable electrode potential-pH diagram for Cu-As-S-Cl-H₂O system at 298 K. All sulfoxy species excluded; dissolved arsenic, chloride, copper and sulfur activities = 10⁻³, 10⁻¹, 10⁻³ and 10⁻⁵, respectively. Dotted lines denote uncertain range of stability of Cu₃As. (Asbjornsson et al., 2003)

Figure 2-4. Eₜₜ-pH diagram of the Cu₃AsS₄-H₂O system at 25 °C for activities of soluble species of Cu, As, and S equal to 0.1. In the figure, S-H₂O equilibria are shown as dashed lines and As-H₂O equilibria as short dashed lines. (Padilla et al., 2008)
2.5 References


Deffreyne, J. and Cabral, T., 2009, “Early Copper Production Results from Vale’s Hydrometallurgical CESL Refinery,” ALTA Copper Conference, Perth, Australia.


3. Reactivity in Alkaline Solutions
R.N. Gow¹, C Young¹, H Huang¹, G Hope², Y Takasaki³

¹Montana Tech of The University of Montana; 1300 W. Park; Butte, MT, 59701, USA
²Griffith University; 170 Kessels Road, Nathan, Qld, Australia, 4111
³Akita University; 1-1 Tegata Gakuen-machi, Akita City, Akita P, Japan 010-8502

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3.1 Abstract

The presence of enargite (Cu₃AsS₄) is problematic in gold processing because it is environmentally hazardous due to its arsenic content but also because it is refractory, causing both cyanide and oxygen consumption to increase. Selective leaching and treatment of the arsenic would prove advantageous prior to applying conventional gold leaching methods. The reactivity of enargite samples from Butte, Montana and Quiruvilca, Peru were spectroelectrochemically studied under alkaline conditions, pH range of 8-13, using Raman spectroscopy and cyclic voltammetry. Raman spectra of the surface were collected during and after voltammograms were potentially cycled in order to determine and compare surface species against theoretical Eₜₐₚ-pH diagrams determined from mass-balanced thermodynamic calculations using STABCAL software. Under slightly oxidizing conditions, covellite (CuS) peaks were found in a short matter of time, above ~100mV vs SHE for pH 9-13, suggesting arsenic leaching specifically occurred. At longer conditioning times, elemental sulfur was observed and tended to passivate the surface. The presence of elemental sulfur suggests that copper was eventually leached from the surface. By operating above pH 12, under slightly reducing conditions near -300mV vs SHE, arsenic can be selectively leached as thioarsenate (AsS₄³⁻) or arsenate (AsO₄³⁻) without sulfur formation.
3.2 Introduction

Environmental limitations on pyrometallurgical processing of ores and concentrates bearing arsenic and other hazardous elements often outweigh those in hydrometallurgical processing, particularly when minerals like enargite (Cu₃AsS₄) are present. Hydrometallurgical processing of enargite-bearing materials can be broken down into two categories: the co-dissolution of arsenic and copper under acidic conditions and the selective leaching of arsenic under alkaline conditions. The selective leaching of arsenic would preferably leave behind copper-rich sulfide phases, typically chalcocite (Cu₂S) and covellite (CuS), which then become more amenable to conventional copper (and gold) processing. Furthermore, selective leaching often employs sulfide (S²⁻), bisulfide (HS⁻) or polysulfides (Sₓ²⁻) to first extract the arsenic as AsS₄³⁻ and AsS₃³⁻ (Delfini et al., 2003; Anderson and Twidwell, 2008; Tongamp et al., 2010a,b). However, hypochlorite leaching (Viñals et al., 2003; Curreli et al., 2005; Mihajlovic et al., 2007), ammonia leaching (Gajam and Raghavan, 1983), and fine-grinding to mechanically activate the enargite surface (Balaz and Achimovicova, 2006) have been investigated to increase the normally slow reaction kinetics. Because gold ores are becoming more refractory due to increasing arsenic contents as a result of enargite, these methods are being examined more closely by the gold-mining industry.

In this study, Raman spectroscopy and cyclic voltammetry were used simultaneously to look at surface reactions of enargite electrodes under alkaline conditions. Specifically, for this study, a spectroelectrochemical technique was used at pH 8-13 with potentials cycled between approximately -1000 and +1000 mV vs SHE. Precise control of these conditions along with various species concentrations will help in understanding how enargite behaves in solution as well as developing a hydrometallurgical separation process. It must be noted that this is the first
in a series of three papers. The second paper (Gow et al., 2014a) covers results obtained under acidic conditions and the third (Gow et al., 2014b) examines alkaline sulfide leaching as one of the more favorable aforementioned hydrometallurgical processes.

3.3 Thermodynamics

A database of standard free energies of formation of species in the Cu-As-S-H\textsubscript{2}O system has been compiled primarily using the MINTEQA2 (Allison, 1991) database but partially supplemented from other sources including the U.S. Geological Survey (Robie, 1984). Results are presented in Table 1. According to Craig and Barton (1973), there are five Cu-As-S sulfosalts; however, only enargite, sinnerite (Cu\textsubscript{6}As\textsubscript{4}S\textsubscript{9}) and tennantite (Cu\textsubscript{12}As\textsubscript{4}S\textsubscript{13}) have listed free energies as also presented in Table 1. They were calculated from the formation equations compiled by Craig and Barton (1973) based on gaseous sulfur (S\textsubscript{2(g)}) but converted herein to base them on elemental sulfur (S\textsubscript{(s)}). It is noted that lautite (CuAsS) and luzonite (Cu\textsubscript{3}AsS\textsubscript{4}) are the other two Cu-As-S sulfosalts but their free energies are unknown (Craig and Barton, 1973). Because enargite and luzonite have the same chemical formula, they have different crystal structures and are referred to as dimorphs. Additional solids for the system have also been identified including Cu(AsO\textsubscript{2})\textsubscript{2} (Nishimura et al. 1993), H\textsubscript{3}AsSO\textsubscript{2} (Helz and Tossell, 2008), and Cu\textsubscript{3}As, which is referred to as the mineral domeykite (Barin, 1995).

STABCAL, a thermodynamic stability calculation program (Young and Huang, 1996; Huang et al., 2005; Huang, 2012), was used to create mass-balanced E\textsubscript{H}-pH diagrams with Cu-As-S molecular ratios of enargite, 0.75:0.25:1 (see Figure 1). Mass balancing constrains thermodynamic calculations, making them more accurate (Gow et al., 2014c) which is critical for ternary and higher order systems. Molecular ratios used to calculate the E\textsubscript{H}-pH diagrams are varied according to the stoichiometries of the other Cu-As-S sulfosalts to determine the roles of
copper, arsenic and sulfur in the stability of various solids, particularly sulfides (Gow et al., 2014d).

There are a few differences in the diagrams when compared to those previously published by Padilla et al. (2008), namely the inclusions of the minerals olivenite (\(\text{Cu}_2\text{AsO}_4\text{OH}\)) and domeykite (\(\text{Cu}_3\text{As}\)). There are also instances of curvature in the equilibrium lines which can only be determined through the mass-balanced calculation method. The curvature indicates a balance between two competing equilibria. In the case of Figure 1B, curvature occurs between enargite (\(\text{Cu}_3\text{AsS}_4\)) and thioarsenate (\(\text{AsS}_4^{3-}\)). Because these diagrams only show the predominant arsenic-containing species, it is not readily apparent that the equilibrium reactions between these two species must also contain arsenate (\(\text{HAsO}_4^{2-}\)) in order to mass balance, according to the following reactions:

\[
\frac{3}{2} \text{H}_2\text{O} + \text{Cu}_3\text{AsS}_4 = \frac{3}{2} \text{Cu}_2\text{S} + \frac{5}{8} \text{AsS}_4^{3-} + \frac{3}{8} \text{HAsO}_4^{2-} + \frac{21}{8} \text{H}^+ \quad \text{Eq. 1}
\]

\[
\frac{6}{8} \text{e}^- + \frac{9}{8} \text{H}_2\text{O} + \text{Cu}_3\text{AsS}_4 = \frac{3}{2} \text{Cu}_2\text{S} + \frac{5}{8} \text{AsS}_4^{3-} + \frac{3}{8} \text{HAsO}_3^- + \frac{3}{2} \text{H}^+ \quad \text{Eq. 2}
\]

Due to the nature of the equations, Eq. 1 is a horizontal line controlled by pH whereas Eq. 2 is an electrochemical reaction where a small amount of arsenic is reduced. By combing the two competing reactions, the curvature becomes apparent.

There are also differences between the two diagrams and are attributed to sulfur oxidation. Figure 1A was created with consideration of sulfate species whereas Figure 1B was created without. In this regard, Figure 1A predicts enargite oxidation to sulfate and Figure 1B predicts oxidation to elemental sulfur. This approach of calculating \(E_{\text{H}^+}\text{-pH}\) diagrams for kinetic purposes has been used extensively in the literature (Huang and Young, 1986; Woods et al., 1987). It should also be noted that the thermodynamic data for metastable copper sulfides were
included in the calculations and they were determined to be stable as thin regions between covellite and chalcocite similar to Woods et al. (1987) and Young et al. (1988); however, their regions of predominance were excluded for easier comprehension of the diagram. The shaded regions in each diagram are areas where solid arsenic species do not exist and would therefore determine conditions where arsenic could be selectively leached. Theoretically, according to these thermodynamic calculations, there is a region where this would occur and, for the most part, it is independent of the sulfur oxidation state and occurs under basic conditions (~pH > 9) but slightly oxidizing (~E_H > -500 mV). Raman spectroscopy and cyclic voltammetry were used in this study to modify and/or confirm the predicted predominance diagrams with the objective to determine if enargite oxidation proceeds to elemental sulfur or goes as far as sulfate (or some other sulfoxy ion).
Table 3.1 - Standard Free Energy Values for Cu-As-S Species.
Primary database used was MINTEQA2 unless otherwise indicated.

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Arsenic (solid)

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<th>Ref</th>
<th>Species</th>
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<td>AsS Realgar</td>
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Copper Arsenic (solid)

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<th>Ref</th>
<th>Species</th>
<th>ΔG° (kcal)</th>
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<td>Cu₃As Domeykite</td>
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<td>Barin</td>
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</table>
Figure 3-1. Mass-balanced $E_h$-pH Diagrams for the Cu-As-S-H$_2$O system as determined for As-containing species ([Cu]=0.075M, [As]=0.025M, [S]=0.10M) A. Oxidation to Sulfate and B. Oxidation to Sulfur. The dashed lines indicate the region of water stability and shaded regions are predominance areas for aqueous species (Small binary regions are not labelled for clarity).
3.4 Materials and Methods

Enargite samples were obtained from Butte, MT and Quiruvilca, Peru. Both samples were characterized with Scanning Electron Microscopy/Mineral Liberation Analysis (SEM/MLA) as shown in Table 2. The Peru sample is ~98% pure with 78% minor antimony (Sb) substitution. By comparison, the Butte sample was ~83% enargite but with only 55% of minor Sb-substitution; however, the sample did contain significant amounts of chalcopyrite (14.5%).

Table 3.2 - SEM/MLA Sample Composition of Enargite Samples

<table>
<thead>
<tr>
<th></th>
<th>Enargite w/ Sb</th>
<th>Enargite</th>
<th>Chalcopyrite</th>
<th>Quartz</th>
<th>Feldspar</th>
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</thead>
<tbody>
<tr>
<td>Butte</td>
<td>54.97</td>
<td>28.09</td>
<td>14.47</td>
<td>2.24</td>
<td>0.23</td>
</tr>
<tr>
<td>Peru</td>
<td>77.93</td>
<td>19.69</td>
<td>0.03</td>
<td>2.35</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Once the samples were characterized, sections with a surface area measuring approximately 0.25 cm² were cut from each. After a copper wire was attached to the back side of the enargite samples using Electrodag 502 and carbon tape, the assemblies were mounted into polytetrafluoroethylene (PTFE) tubing and then sealed in the tubing using a non-conductive epoxy resin. Conductivity measurements showed the mineral electrodes were conductive and therefore ready to be used in for the spectroelectrochemical studies. Raman spectra and cyclic voltammograms collected from the two electrodes yielded the same results and were virtually indistinguishable. Consequently, it did not need to be reported which results were obtained from which sample/electrode. In between these spectroelectrochemical measurements, the exposed face was polished with 200-grit SiC sandpaper and cleaned with de-ionized water.

Raman studies were conducted at Griffith University in Brisbane, Australia. In-situ studies were conducted using a Renishaw Raman 100 InVia spectrophotometer. The system has a 100-mW He-Ne laser as the excitation source (632.8 nm), a MultiPhysics 1000-line grating, 2 Rayleigh-scatter filters, and a 256x512 CCD array as the detector. Raman spectra were
calibrated using the 520 cm\(^{-1}\) primary band of pure silicon. The system programming was controlled by the GRAMS spectrometer software suite. Because of the selected optics, detection of peaks below 200 cm\(^{-1}\) was not entirely reliable and, as a result, peak characterization was presumably conducted on the less intense peaks at higher wavenumbers. The pH was controlled by buffers that were created according to the CRC Handbook (Haynes, 2011). The buffers included borate for pH 8 and 9, bicarbonate for pH 10 and 11, and chloride for pH 12 and 13. No buffer effects were observed in any of the experiments.

Ex-situ spectra were collected using a Renishaw Raman RM2000 InVia spectrophotometer, also with a 632.8 nm HeNe laser, using a Peltier-cooled CCD detector. The attached Leica LMDM microscope allows for a rapid visual inspection of the electrode surface with up to 600x magnification. Because the enargite electrodes and surface species were easily burned under full laser intensity, the power was reduced to 10\% or less. In addition, the number of scans was increased to 5 with >10 second exposure to maximize the Raman signal. The system was controlled by the Renishaw WiRE 3.2 software package.

3.4.1 Static Tests

Initially, the pH and potential conditions were held constant for various defined points of interest on the Cu-As-S E\(_{HJ}\)-pH diagram while spectra were collected for up to 24 hrs. These tests were used to identify Raman peak positions of the major mineral phases. The electrodes were held under potentiostatic control until removed from the solution and then dried under nitrogen gas. Spectra of the surface were collected with the RM2000 at 10\% laser power.

3.4.2 Multifiles

The multifiles combine a continuously scanning program for the collection of Raman spectra which occurs every five seconds and are linked to the cyclic voltammograms. The
electrodes were cycled three times, scanning initially in either the negative or positive directions but typically at a scan rate of 5 mV/sec between -1000 and +1000 mV. There is a time delay between changes in the current density slope and when the Raman detected composition changes in order to maximize Raman signals. However, it is noted that the Raman spectra are therefore collected over a range of potentials. In this regard, slow scan rates or constant potentials are preferred so that the Raman spectra can be linked to the voltammograms, and therefore the E
H
-pH diagrams, as best as possible.

For cyclic voltammetry, solutions were contained in a 5-port electrochemical cell. The cell was clipped into a holding bracket, which allowed horizontal and vertical adjustment to center the focal point of the laser. The port closest to the laser was used for the enargite electrode while the others were used for the Ag/AgCl saturated KCl (+0.197 mV vs SHE) reference electrode and a platinum counter electrode. As the enargite electrodes tested were interchangeable, and their surface areas were not exact, voltammograms are scaled by current (A) instead of current density (A/m²). Potentials at which reactions occur are plotted against the mass balanced E
H
-pH diagrams for reaction determination instead of identification using peak areas.

3.5 Raman Spectroscopy

The reference peaks for enargite appear at 265, 338, 384, 679 and 725 cm⁻¹ (see Figure 2). For consistency, these spectra and others were compared against the RRUFF Raman mineral spectroscopic database (Downs, 2006). Tennantite (Cu₁₂As₄S₁₃), chalcocite (Cu₂S), covellite (CuS), olivenite (Cu₂AsO₄OH), elemental copper, elemental sulfur, and pyrite (FeS₂) were identified in this manner. Copper (II) hydroxide formation was identified via precipitation during testing. Tennantite was identified by the reversal of peak intensities for peaks at 338 and
384 cm$^{-1}$, although it did not completely reflect the spectra in the Raman database. There are no known spectra for sinnerite or lautite, and none of the experimental results could be attributed to them based on common bonds.

Sulfur on enargite was identified first at pH 9 and 0 mV vs SHE as shown in Figure 3. The reference peaks for elemental sulfur at 150, 220 and 470 cm$^{-1}$ are included for comparison. Surface spectra usually indicated a CuS phase, often with a characteristic peak at 470 cm$^{-1}$ before the sulfur peaks would build in intensity. The presence of sulfur was followed by a drop in current density which then indicated no further reaction occurring and likely passivation of the surface.

3.6 Cyclic Voltammetry

Cycling the electrode potential gave relatively the same pattern of voltammograms, independent of cycle number. A typical example is shown in Figure 4 for voltammograms obtained at pH 8 at a scan rate of 5 mV/sec with an initial potential of -200 mV and lower and upper potentials of -1200 and + 800 mV vs sat. Ag/AgCl (+197 mV vs SHE), respectively.
Figure 3-2. Raman spectra of the solid enargite electrodes used in this study

Figure 3-3. Sulfur Growth on Enargite Surface (pH 9, 0 mV, 60 min)
In this example, resulting peaks on the cathodic scan suggest enargite reduces to tennantite, where the arsenic is partially reduced from its +5 state to +3. Further reduction of the surface converts to chalcocite and finally elemental copper as depicted in the following reduction reactions and observed from the Raman spectra collected simultaneously:

\[
4\text{Cu}_3\text{As}_4\text{S}_4 + 3\text{H}^+ + 6\text{e}^- = \text{Cu}_{12}\text{As}_4\text{S}_{13} + 3\text{HS}^- \quad E^0 = -0.195 \quad \text{Eq. 3 (C1)}
\]

\[
\text{Cu}_{12}\text{As}_4\text{S}_{13} + \text{H}^+ + 2\text{e}^- = \text{Cu}_6\text{As}_4\text{S}_9 + 3\text{Cu}_2\text{S} + \text{HS}^- \quad E^0 = -0.208 \quad \text{Eq. 4 (C2a)}
\]

\[
\text{Cu}_6\text{As}_4\text{S}_9 + 2\text{H}^+ + 4\text{e}^- = 3\text{Cu}_2\text{S} + 4\text{AsS} + 2\text{HS}^- \quad E^0 = -0.258 \quad \text{Eq. 5 (C2b)}
\]

\[
\text{Cu}_2\text{S} + \text{H}^+ + 2\text{e}^- = 2\text{Cu}^0 + \text{HS}^- \quad E^0 = -0.525 \quad \text{Eq. 6 (C3)}
\]

It is noted that domeykite (\(\text{Cu}_3\text{As}\)) was not observed as predicted thermodynamically in the \(E_\text{H}-\text{pH}\) diagrams presented earlier in Figures 1A and 1B. In this regard, an \(E_\text{H}-\text{pH}\) diagram will be re-determined without considering domeykite as presented and discussed later. On the other hand, sinnerite (\(\text{Cu}_6\text{As}_4\text{S}_9\)) was also not observed but will not be excluded from
consideration because it is expected that its stability range will be narrow and may not be
detected spectroelectrochemically. Consequently, resulting tennantite may reduce to form
sinnerite as an intermediate product as shown with Reactions C2a and C2b. Unfortunately,
Raman spectra could not confirm realgar (AsS) or orpiment (As$_2$S$_3$) as reaction products but
Reaction C2b is the only thermodynamically acceptable prediction.

After reversing the scan direction, Figure 4 also reveals anodic peaks which correspond
to copper oxidation to chalcocite, then covellite, and finally copper hydroxide and sulfur as
depicted in the following oxidation reactions and observed from the Raman spectra collected
simultaneously:

\[
\begin{align*}
2\text{Cu}^0 + \text{HS}^- & = \text{Cu}_2\text{S} + \text{H}^+ + 2e^- \quad \text{E}^0 = -0.525 \quad \text{Eq. 7} \quad (A1) \\
\text{Cu}_2\text{S} + \text{HS}^- & = 2\text{CuS} + \text{H}^+ + 2e^- \quad \text{E}^0 = -0.142 \quad \text{Eq. 8} \quad (A2) \\
\text{CuS} + 2\text{H}_2\text{O} & = \text{Cu(OH)}_2 + \text{S}^0 + 2\text{H}^+ + 2e^- \quad \text{E}^0 = 0.885 \quad \text{Eq. 9} \quad (A3a)
\end{align*}
\]

Interestingly, not only were the two sulfides spectroelectrochemically observed but so was cupric
hydroxide (Cu(OH)$_2$) precipitate. It has been noted that copper hydroxide solubilizes in borate,
(Young et al., 1988) which is present in the buffer solutions at this pH. This could explain why
olivenite (Cu$_2$AsO$_4$OH) was also periodically observed albeit in more significant amounts at pH
9 which is also comprised of a borate buffer. Olivenite was not observed until potentials reached
~500 mV vs SHE. In this regard, it is suggested that anodic reaction A3 also be represented as:

\[
2\text{CuS} + \text{AsO}_4^{3-} + \text{H}_2\text{O} = \text{Cu}_2\text{AsO}_4\text{OH} + 2\text{S}^0 + \text{H}^+ + 4e^- \quad \text{E}^0 = 0.376 \quad \text{Eq. 10} \quad (A3b)
\]

such that the arsenate (AsO$_4^{3-}$) likely comes from the oxidation of realgar (AsS):

\[
\text{AsS} + 4\text{H}_2\text{O} = \text{AsO}_4^{3-} + \text{S}^0 + 8\text{H}^+ + 5e^- \quad \text{E}^0 = 0.683 \quad \text{Eq. 11} \quad (A4)
\]

where realgar is presumed to be present as a result of cathodic reaction C2b. However, it is also
conceivable that enargite itself oxidizes to arsenate and precipitates out as olivenite and covellite:
\[
\text{Cu}_3\text{AsS}_4 + 5\text{H}_2\text{O} = \text{Cu}_2\text{AsO}_4\text{OH} + \text{CuS} + 3\text{S}^0 + 9\text{H}^+ + 9\text{e}^- \quad E^0 = 0.572 \quad \text{Eq. 12 (A5)}
\]

Because Raman spectra showed elemental sulfur (\(\text{S}^0\)) formed at each of the pH values investigated in this study, Reactions A3-A5 are all written with it as a product. Enargite oxidizes to elemental sulfur, at least in the time frames examined in this study, and not sulfate. Consequently, the \(E_\text{H}\)-pH diagram that will be redetermined, discussed and presented in the next section will only consider oxidation to elemental sulfur and not sulfate.

It is important to note that these results strongly show that arsenic can be leached from enargite to form covellite and elemental sulfur. Periodically, the sulfur could not be observed until more than 1 cycle was conducted allowing for enough to accumulate. When that happened, the surface was observed to passivate. More importantly, the sulfur tended to accumulate more at pH’s above 10 where enargite is not stable. Under these conditions, enargite could not be regenerated during the voltammetric studies. However, when the pH was below 10, the enargite surface tended to regenerate as evidenced by the cathodic peak C4 in Figure 4 but more species than just enargite were observed.

### 3.7 Updated Thermodynamics

Based on the spectroelectrochemical results just presented, some modifications have been made to the \(E_\text{H}\)-pH diagrams in Figure 1. Consequently, olivenite and sinnerite will continue to be considered and domeykite (\(\text{Cu}_3\text{As}\)), cuprite (\(\text{Cu}_2\text{O}\)) and tenorite (\(\text{CuO}\)) will not. Furthermore, in regards to kinetics, only sulfide oxidation to elemental sulfur was allowed, so sulfoxyl ions such as sulfate were not considered.

The resulting mass-balanced \(E_\text{H}\)-pH diagram is shown in Figure 5. A comparison to Figure 1B shows that, by not considering domeykite, elemental copper becomes stable under the reducing conditions and both covellite and chalcocite stability regions increase. In addition, by
not considering the copper oxides, olivenite has a larger stability region that increases from pH 9 to 11. The region that copper and arsenic can be separated by leaching is reduced and helps explain why sulfide leaching (including bisulfide and polysulfide leaching) is usually restricted to alkaline conditions at least > pH 11, and typically > pH 12 to insure selective leaching would occur. Furthermore, selectivity will be best achieved if the copper remains present as a solid sulfide, either as covellite or chalcocite, such that elemental sulfur formation would be prevented in order to avoid surface passivation and the risk of incomplete leaching. In this regard, leaching conditions should be kept > pH 12 with $E_{\text{H}}$ between approximately -600 mV where thioarsenate ($\text{AsS}_3^{2-}$) is stable and +100 mV where arsenate ($\text{AsO}_4^{3-}$) is stable.

All voltammograms were then re-examined for inflection points in which increased current flow was observed thereby indicating an electrochemical reaction was starting to occur. The potentials where reactions occurred were plotted on the updated $E_{\text{H}}$-pH diagram and results are presented in Figure 6. Clearly, the potentials line up well with thermodynamic expectations and much better than would occur in Figure 1B. This suggests the diagram is accurate giving high confidence for the results presented in this study. It is noted that a series of points occur near 0 mV vs SHE at pH 10-13 and are attributed to the formation of nonstoichiometric copper sulfides (Young et al. 1988) as chalcocite oxidizes to covellite. These points are not observed at lower pH values because chalcocite is not stable under these conditions (in the presence of arsenic). As noted earlier, the nonstoichiometric copper sulfides were stable according to the thermodynamic calculations but were not included in the $E_{\text{H}}$-pH diagrams in Figures 1A, 1B, 5 and 6 for clarity purposes.
Figure 3-5. Updated $E_{H^+}$pH Diagram for the Cu-As-S system with Region of Selective Leaching. The dotted line indicates the regions of water stability, copper-only transitions are indicated by the dashed line, and area above the bold line indicates stability of elemental sulfur.

Figure 3-6. Updated $E_{H^+}$pH Diagram overlaid with CV inflection points.
3.8 Conclusions

Enargite (Cu₃AsS₄) electrodes were spectroelectrochemically studied under alkaline conditions at a pH range of 8-13 using Raman spectroscopy and cyclic voltammetry simultaneously in order to determine and compare surface species against theoretical Eₜ-H-pH diagrams determined from mass-balanced thermodynamic calculations. Under slightly oxidizing conditions, covellite (CuS) peaks were found in a short matter of time, above ~100mV vs SHE for pH 9-13, suggesting arsenic leaching specifically occurred. At higher potentials and longer conditioning times, elemental sulfur was observed and tended to passivate the surface. The presence of sulfur suggests that copper was eventually leached. By operating above pH 12, under slightly reducing conditions, elemental sulfur formation would be avoided between approximately -700 mV vs SHE where thioarsenate (AsS₄³⁻) forms and +100 mV vs SHE where thiosulfate (AsO₄³⁻) forms. An average potential near -300 mV vs SHE is therefore suggested to selectively leach arsenic from enargite and form covellite or chalcocite. Spectroelectrochemical results match up very well with a newly calculated mass-balanced Eₜ-H-pH diagram.
3.9 References


4. Reactivity in Acidic Solutions

R.N. Gow¹, C Young¹, H Huang¹, G Hope²

¹Montana Tech of The University of Montana; 1300 W. Park; Butte, MT, 59701, USA
²Griffith University; 170 Kessels Road, Nathan, Qld, Australia, 4111

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4.1 Abstract

Acidic treatment of enargite (Cu₃AsS₄) dissolves both arsenic and copper from the mineral. Attempts can then be made to separate them in the pregnant leach solution. The reactivity of enargite was examined in acidic to neutral solutions, over the pH range 1-7, to determine a potential range for co-dissolution. Enargite mineral samples from Butte, MT and Quirivilca, Peru were used as working electrodes in a cyclic voltammetry corrosion cell setup, which were then cycled multiple times over -1000 to 1000 mV. Surface reactions and transitions were characterized using in-situ Raman spectroscopy, which were then compared to updated EₜH-pH diagrams for the copper-arsenic-sulfur-water system from a previous study done under alkaline conditions. The region of co-dissolution is limited to > 600 mV vs. SHE and pH < 1 under the proposed diagram.
4.2 Introduction

Recent reviews (Lattanzi et al., 2008; Safarzadeh et al., 2012a, b) have summarized studies looking into the modelling and optimization of the recovery of metal content from enargite, Cu$_3$AsS$_4$. The necessary drive to push towards a hydrometallurgical process, as arsenic regulations become stricter and easy-to-process copper/copper-gold deposits become scarce, has allowed for a vast number of studies. Processing techniques can be broken into acidic and alkaline leach process strategies including the prospect of bioleaching which has been more frequently examined recently.

Alkaline leaching attempts to selectively leach arsenic from enargite while leaving behind a solid, copper-sulfide phase that could be treated more conventionally (Gow et al., 2014a). Acidic leaching of enargite dissolves both copper and arsenic although quite slowly. Attempts to optimize the leach kinetics have included characterization of the copper and arsenic dissolution mechanisms over various pH conditions (Cordova et al., 1997; Asbjornsson et al., 2004; Sasaki et al., 2010), and with the addition of various oxidants, Fe$^{3+}$ (Dutrizac et al., 1972; Elsener et al., 2007; Fantauzzi et al., 2007; Padilla et al., 2010) or Cl$_2$/Cl$^-$ (Herreros et al., 2002), or at increased temperature and pressures (Padilla et al., 2008 and 2010).

There is a general consensus that the kinetics are dominated by a surface-controlled reaction due to a porous, sulfur-rich layer that forms at the enargite surface which is relatively unchanged by agitation. The composition of this layer is in question as to whether it is an elemental sulfur growth formed from the release of copper and arsenic into solution or, instead, a metal-depleted sulfide layer. X-Ray photoelectron (XPS), X-ray excited Auger Electron (XAES) (Fantauzzi et al., 2007). Raman Spectroscopic techniques (Asbjornsson et al., 2004) have been incorporated to characterize the enargite surface oxidation species in conjunction with previous
work along with thermodynamic expectations as typically determined by speciation calculations such as E\textsubscript{H-PH}/Pourbaix diagrams (Gow et al., 2014a).

This study includes an in-depth thermodynamic study coupled with in-situ Raman Spectroscopy and cyclic voltammetric techniques, over the pH range 1-7, to better predict and identify surface oxidation species. Electrodes were created from natural mineral samples, and used for both static and cyclic voltammetric testing.

4.3 Thermodynamics

Similarly to the study of enargite’s reactivity in alkaline solution (Gow et al., 2014a), a thermodynamic database of species in the Cu-As-S-H\textsubscript{2}O system was compiled. StabCal, a thermodynamic stability calculation program (Huang et al., 2005 and 2011), was used to create mass-balanced E\textsubscript{H-PH} diagrams under acidic conditions using the Cu-As-S molar ratio for enargite, 0.75:0.25:1 at a total Cu concentration of 0.75M. Stability calculations were completed for complete oxidation to sulfate (see Figures 1A and 1B) and for oxidation to elemental sulfur only (see Figures 1C and 1D). Selected regions are shaded where only soluble species exist. CAS ratios are varied to show the importance of the mass-balanced calculations to more complicated systems but will be reported elsewhere (Gow et al., 2014c, d).

The proposed diagrams differ from those determined by Asbjornsson (2004) and Padilla et al. (2007). The concentration ratio of the dissolved species considered by Asbjornsson (2004) was 100:10:1 for Cu:As:S, respectively. Chlorine was also included at 100x the activity of copper. Under these conditions, copper and arsenic species were found to be soluble below pH 5 at an oxidizing potential of 400mV. The E\textsubscript{H-PH} diagram presented by Padilla et al. (2007) suggests that the co-dissolution range existed up to approximately pH 4 and varied between 350 and 400 mV. The dominant species were determined to be Cu\textsuperscript{2+}, H\textsubscript{3}AsO\textsubscript{4}/H\textsubscript{2}AsO\textsubscript{3}\textsuperscript{-} and HSO\textsubscript{4}\textsuperscript{-}.
/SO_{4}^{2-}\) assuming a 1:1:1 CAS ratio. Neither of these situations reflects the composition of the enargite surface and, as previously mentioned, the mass-balanced compositions can significantly alter the expected outcome. In the \(E_{\text{H}}\)-pH diagrams produced for this study, the apparent overlap of arsenic and copper dissolution shrinks to > 500 mV vs. SHE at pH < 3 when full oxidation to sulfate is considered. This region decreases to > 600 mV vs. SHE and pH < 1 when only partial oxidation to elemental sulfur is considered.

Several species have also been included that have not appeared elsewhere in thermodynamic considerations, particularly olivenite \((\text{Cu}_{2}\text{AsO}_{4}\text{OH})\) and domeykite \((\text{Cu}_{2}\text{As})\). Several notable copper sulfate hydroxide species, brochantite \([\text{CuSO}_{4}\cdot3\text{Cu(OH)}_{2}]\) and antlerite \([\text{Cu}_{3}\text{(SO}_{4}\cdot\text{(OH)}_{4}]\), are also stable but not labelled to keep the diagrams easier to read. Their stability regions occur similarly with olivenite which was identified during the Raman spectroscopic study of enargite in moderate alkaline solutions (Gow et al., 2014a). At a higher pH, > 11, enargite was shown to be selectively leached of its arsenic content.

### 4.4 Sample Analysis

Natural enargite samples from Butte, MT and Quiruvilca, Peru were used interchangeably in the CV and Raman spectroscopy. Both were characterized using scanning electron microscopy (SEM), mineral liberation analysis (MLA), and X-ray diffraction (XRD) previously (Gow et al., 2014a). Although the Butte sample included a significant amount of chalcopyrite (see Table 1), there were no distinguishable differences in the CVs or Raman spectra that were obtained between the two samples.

<table>
<thead>
<tr>
<th>Table 4.1 - Mineralogical Composition of Enargite Samples</th>
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<tbody>
<tr>
<td><strong>Butte</strong></td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td><em>Peru</em></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
4.5 Raman Spectroscopy

Raman studies were conducted at Griffith University in Brisbane, Australia. In-situ studies were conducted using a Renishaw Raman 100 InVia spectrophotometer. The system has a 100-mW He-Ne laser as the excitation source (632.8 nm), a MultiPhysics 1000-line grating, 2 Rayleigh-scatter filters, and a 256x512 CCD array as the detector. The Raman spectrometer was calibrated using the 520 cm$^{-1}$ primary band of pure silicon. The system programming was controlled by the GRAMS spectrometer software suite. Detection of peaks below 200 cm$^{-1}$ was not entirely reliable, requiring other, possibly less intense, peaks for characterization.

Initially, the mineral electrode surface was held at a given potential based on points of interest on the E$_{H}$-pH diagram. Buffer solutions, created according to the CRC Handbook in the range of pH 1-7, were contained in a 5-port electrochemical cell. The cell allowed for horizontal and vertical adjustment to center the focal point of the laser. The port closest to the laser was used for the enargite electrode; while the others were used for the Ag/AgCl saturated KCl (+197mV vs SHE) reference electrode and a platinum counter electrode.

Spectra were collected for up to 24 hours, and used, in addition to the spectra of the RRUFF database (Downs, 2006), to determine characteristic peaks for potential species. Static ex-situ spectra were done using a Raman InVia spectrometer, controlled by the Renishaw WiRE 3.2 software package. Between tests, the surface was polished with 200 grit SiC paper and cleaned with de-ionized water. Results from the characterization testing were tabulated in Table 2.
Figure 4-1. Mass-balanced $E_{H}$-pH Diagrams for the Cu-As-S system
A. Copper species, Oxidation to Sulfate; B. Arsenic species, Oxidation to Sulfate; C. Copper species, Oxidation to Sulfide; D. Arsenic species, Oxidation to Sulfide. The included dashed line indicates the region of water stability. Small binary regions are not labelled for clarity.
4.6 Cyclic Voltammetry Confirmation

Cyclic voltammetry tests were conducted in the same electrochemical cell, in conjunction with a Raman multifile program. The multifile program combines a continuously scanning program, taking a spectrum every five seconds. The mineral electrodes were cycled positively from 0mV vs SHE to an upper limit of +1000mV, then to a lower limit of -1000mV for a total of three cycles. Negative scanning cycles were performed next, in a similar manner.

An example voltammogram at pH 2 is shown in Figure 2. Oxidation occurs at anodic peaks $A_1$, at approximately 300mV and $A_2$, at approximately 480mV. These correspond to the following transitions, Eq. 1 and 2, predicted by Figures 1C and 1D:

\[
\begin{align*}
2 \text{Cu}_3\text{AsS}_4 + 3 \text{H}_2\text{O} &\rightarrow 6 \text{CuS} + \text{As}_2\text{O}_3 + 2 \text{S}^0 + 6 \text{H}^+ + 6 \text{e}^- & \text{[Eq.1]} \\
\text{As}_2\text{O}_3 + 5 \text{H}_2\text{O} &\rightarrow 2 \text{H}_3\text{AsO}_4 + 4 \text{H}^+ + 4 \text{e}^- & \text{[Eq.2]}
\end{align*}
\]

Figure 4-2. Voltammogram of enargite at pH 2, scanning positively from 0mV vs SHE at 5mV/s scan rate and cycled three times between +1000mV and -1000mV.
Copper arsenate or sulfate species, such as olivenite (\(\text{Cu}_2\text{AsO}_4\text{OH}\)), that were observed under alkaline conditions (Gow et al., 2014a) were not detected via Raman during the multifile program run.

As the electrode is cycled back negatively, a series of peaks/shoulders appear at \(C_1\) suggesting reactions involving the copper-arsenic sulfosalt series, enargite to tennantite (\(\text{Cu}_{12}\text{As}_4\text{S}_{13}\)) to sinnerite (\(\text{Cu}_6\text{As}_4\text{S}_9\)), occur and correspond to the following reactions, Eq. 3 and 4:

\[
4 \text{Cu}_3\text{AsS}_4 + 6 \text{H}^+ + 6 \text{e}^- \rightarrow \text{Cu}_{12}\text{As}_4\text{S}_{13} + 3 \text{H}_2\text{S} \quad [\text{Eq. 3}]
\]

\[
\text{Cu}_{12}\text{As}_4\text{S}_{13} + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Cu}_6\text{As}_4\text{S}_9 + 3 \text{Cu}_2\text{S} + \text{H}_2\text{S} \quad [\text{Eq. 4}]
\]

During this experiment, both chalcocite (\(\text{Cu}_2\text{S}\)) and tennantite were identified, as shown by the Raman spectrum in Figure 3. In this regard, it is concluded that domeykite is not a reduction product thereby confirming observations from alkaline studies (Gow et al., 2014a).

![Figure 4-3 - Enargite sample at pH 2, scanning positively from -0mV vs SHE, 5mV/s scan rate.](image)
## Table 4.2 - Raman Characteristic Peak Positions

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Formula</th>
<th>Peaks (cm(^{-1}))</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Potential Species</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enargite</td>
<td>Cu(_3)AsS(_4)</td>
<td>269 338/381</td>
<td></td>
</tr>
<tr>
<td>Tennantite</td>
<td>Cu(<em>{12})AsS(</em>{13})</td>
<td>345/388</td>
<td></td>
</tr>
<tr>
<td>Domeykite</td>
<td>Cu(_3)As</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>470</td>
<td></td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Cu(_2)S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Cu(_2)S</td>
<td>220 290</td>
<td>400 600 1000</td>
</tr>
<tr>
<td>Orpiment</td>
<td>As(_2)S(_3)</td>
<td>200 290 310/350</td>
<td></td>
</tr>
<tr>
<td>Realgar</td>
<td>AsS</td>
<td>220 350</td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>S</td>
<td>150 220 440/470</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>150 300 530 620</td>
<td>RRUFF</td>
</tr>
<tr>
<td>Brochantite</td>
<td>Cu(_2)SO(_4)(OH)(_6)</td>
<td>380 610 980</td>
<td>RRUFF</td>
</tr>
<tr>
<td>Antlerite</td>
<td>Cu(_2)SO(_4)(OH)(_4)</td>
<td>420/440 980</td>
<td>RRUFF</td>
</tr>
<tr>
<td>Cornwallite</td>
<td>Cu5(AsO(_4))2(OH)(_4)</td>
<td></td>
<td>RRUFF</td>
</tr>
<tr>
<td>Olivenite</td>
<td>Cu(_2)AsO(_4)(OH)</td>
<td>150 220 286</td>
<td>853/957</td>
</tr>
<tr>
<td><strong>Mineral Gangue</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS</td>
<td>350 388</td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>SiO(_2)</td>
<td>210 468</td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS(_2)</td>
<td>290 480</td>
<td></td>
</tr>
<tr>
<td><strong>Nonstoichiometric Sulfides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Djurleite</td>
<td>Cu(_{1.98})S</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>Digenite</td>
<td>Cu(_{1.4})S</td>
<td></td>
<td>RRUFF</td>
</tr>
<tr>
<td>Roxbyite</td>
<td>Cu(_{1.76})S</td>
<td></td>
<td>RRUFF</td>
</tr>
<tr>
<td>Anilite</td>
<td>Cu(_{1.75})S</td>
<td>470</td>
<td>RRUFF</td>
</tr>
<tr>
<td>Yarrowite</td>
<td>Cu(_{1.2})S</td>
<td>210 280 390</td>
<td>RRUFF</td>
</tr>
<tr>
<td>Villamaninite</td>
<td>CuO(_{0.3})S</td>
<td>470</td>
<td>RRUFF</td>
</tr>
<tr>
<td><strong>Arsenates</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arsenate</td>
<td>Na(_3)AsO(_4)</td>
<td>155 335/372</td>
<td>726</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Na(_3)SO(_4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monothio-</td>
<td>AsSO(_3^+)</td>
<td>163 371 432</td>
<td>797</td>
</tr>
<tr>
<td>Di-</td>
<td>AsS2O(_2^+)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tri-</td>
<td>AsS(_2^+)O(_4^-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetra-</td>
<td>AsS(_4^+)</td>
<td>390 580</td>
<td></td>
</tr>
</tbody>
</table>

**Bold** denotes major peak  
**Italic** denotes broad peak
Unfortunately, there are no characteristic Raman peaks for sinnerite (see Table 2), as it is a unique mineral that has not yet been included in the RRUFF database. However, its formation is not excluded; rather, it is understood that, because its expected stability range will be narrow, it may not yield sufficiently strong, identifiable peaks to be detected. Consequently, resulting tennantite (see Eq. 3) may reduce to sinnerite and some chalcocite (see Eq. 4) or react completely to chalcocite as shown in Eq. 5:

$$\text{Cu}_{12}\text{As}_4\text{S}_{13} + 14 \text{H}^+ + 14 \text{e}^- \rightarrow 4 \text{As}^0 + 6 \text{Cu}_2\text{S} + 7 \text{H}_2\text{S} \quad [\text{Eq. 5}]$$

Likewise, sinnerite, if produced, will likely react similarly to produce more chalcocite:

$$\text{Cu}_6\text{As}_4\text{S}_9 + 12 \text{H}^+ + 12 \text{e}^- \rightarrow 4 \text{As}^0 + 3 \text{Cu}_2\text{S} + 6 \text{H}_2\text{S} \quad [\text{Eq. 6}]$$

The last cathodic peak identified as $C_2$ in Figure 2 occurs at approximately $-420$ mV at pH 2. Measurements across the acidic range tested showed the potentials followed the general trend:

$$C_2 = -300 \text{mV} - 60 \text{mV} \times [\text{pH}] \quad [\text{Eq. 7}]$$

with approximately $-360$ mV determined for pH 1 and $-720$ mV for pH 7. The $-60$ mV slope is close enough to the theoretical slope of $-59.15$ mV. It also suggests the reduction reaction contains equal protons ($\text{H}^+$) and electrons ($\text{e}^-$).

If domeykite is not considered in the $E_{\text{H}}$-pH diagram, this line follows the expected transition from chalcocite ($\text{Cu}_2\text{S}$) to elemental copper in agreement with Young et al. (1987):

$$\text{Cu}_2\text{S} + 2 \text{H}^+ + 2 \text{e}^- \rightarrow 2 \text{Cu} + \text{H}_2\text{S} \quad [\text{Eq. 8}]$$

It is important to point out that the reduction reaction shown in Equation 8 does have equal numbers of protons and electrons as do the reduction reactions illustrated in Equations 3-6. Elemental sulfur appeared in all experiments but only under oxidizing conditions. Raman spectra showed peaks at 650 mV at pH 1, 500 mV at pH 2, 750 mV at pH 3-4, and 650 mV at pH 5-7. These potentials do not match well with the $E_{\text{H}}$-pH diagrams in Figure 1 but clearly show that
enargite oxidation proceeds only as far as sulfur (Figures 1C and 1D) and not to sulfate (Figures 1A and 1B). Furthermore, the sulfur peaks only appeared during the first cycles of each test, which is attributed to the formation of aqueous H$_2$S under reducing conditions (Eq. 3-6 and 8) and its subsequent loss to the electrode system either due to diffusion or stirring from the enargite surface or its inability to react in reverse, at least under the time and conditions used.

4.7 Updated Thermodynamics

Based on the CVs collected and the Raman Spectroscopy results obtained in this study, the E$_{H}$-pH diagram in Figure 4 is proposed. This diagram includes an expected co-dissolution range limited by Figure 1C, bounded by the limitations of copper dissolution under the thermodynamic conditions for oxidation to elemental sulfur only. The reduction species of enargite are limited to elemental arsenic (As$^0$) and chalcocite (Cu$_2$S), which varies from previous literature. Padilla (2005) and Asbjornsson (2004) both include arsine gas in their calculations which is not expected to occur due to the presence of sulfides, at least under the conditions examined. Chalcocite and tennantite were identified but arsenic bearing species, which are more difficult to determine via Raman, were not. Hence, the formation of As$^0$, As$_2$O$_3$ and H$_3$AsO$_4$, for example, were inferred based on thermodynamics but also to balance the proposed electrochemical reactions. Domeykite, as already noted, was eliminated from consideration.

All inflection points from the CVs are plotted against the updated E$_{H}$-pH diagram as shown in Figure 5. They fall in line with the expected sulfur transition points, as well as the transitions between chalcocite and elemental copper instead of domeykite. The rough cathodic peaks corresponding to C$_1$, occurring over a broad range, are likely due to the transition between the copper-arsenic sulfosalts, as chalcocite is separated from the surface species, increasing the arsenic to copper and sulfur ratios. There are also a series of points from pH 3-5 that exist at
approximately -700 mV. Raman static testing of this area shows peaks consistent with a copper phthalate formation, occurring from an interaction of elemental copper on the mineral surface with the buffer, potassium hydrogen phthalate, which is only used for those pH values.

Finally, it is important to point out that, under acidic conditions, enargite oxidation proceeds to covellite (CuS) and consequently no metastable copper sulfides are observed, as was the case under oxidizing conditions when chalcocite was an oxidation product (Gow et al., 2014a). The region of covellite stability is also the region where selective arsenic leaching could be performed. Potentials must be kept below olivenite stability and in the region of stability of aqueous arsenites and arsenates. This region is narrow under highly acidic conditions (i.e., 400-600mV at pH 2) and somewhat larger under less acidic conditions (i.e., 100-500mV at pH 6). The issues will be controlling the potential and pH to meet these conditions and obtaining appropriate leaching kinetics.

4.8 Conclusions

The reactivity of enargite, in conjunction with the previous study (Gow et al., 2014a, has now been spectroelectrochemically examined, over the pH range 1-13. A thorough thermodynamic study has been compared against Raman spectroscopic results of the surface reaction species during voltammetric testing. The spectra from the CV testing and Raman characterization were plotted against mass-balanced E<sub>th</sub>-pH diagrams, generated by StabCal based on the stoichiometric ratio of enargite. Excellent correlations were observed; although, there was some scatter with the CV testing.

The final proposed diagram did not include sulfate species. Domeykite, the copper arsenide mineral Cu<sub>3</sub>As, was also removed from consideration in both studies. Under reducing conditions, the enargite surface showed a transition to tennantite (Cu<sub>12</sub>AsS<sub>13</sub>), then elemental
arsenic ($\text{As}^0$) and chalcocite with a possible intermediate of sinnerite ($\text{Cu}_6\text{As}_4\text{S}_9$), and finally elemental copper. Under oxidizing conditions, covellite ($\text{CuS}$) was produced along with $\text{As}_2\text{O}_3$ or soluble arsenites and arsenates depending on the pH. At higher potentials, the covellite solubilized as cupric ($\text{Cu}^{2+}$) cation $< \text{pH 1.5}$ or precipitated as olivenite ($\text{Cu}_2\text{AsO}_4\text{OH}$) $> \text{pH 1.5}$. In this regard, co-dissolution of copper and arsenic is limited to potentials $> 600\text{mV}$ and $\text{pH} < 1.5$. Likewise, the region for arsenic dissolution is limited to region where $\text{CuS}$ is stable along with arsenate and arsenite. Consequently, the potential range varies considerably with pH: at pH 2, it is 400-600mV and at pH 6, it is 100-500mV.

Based on the spectroelectrochemical data, the proposed update to the $E_{\text{H}}$-$\text{pH}$ diagram provides a more complete understanding of the system. This series of work is added to the reactivity of enargite in an alkaline leach system (Gow et al., 2014a), and will continue with the addition of a bisulfide lixiviant (Gow et al., 2014b).

4.9 Acknowledgements

The authors would like to thank Newmont Mining for their financial support. Mineral samples were provided by DJ Minerals of Butte, MT and Mineral Zone of Tucson, Az.
Figure 4-4. Updated $E_{m}$-pH Diagram for the Cu-As-S system with Region of co-dissolution. The dotted line indicates the regions of water stability, copper-only transitions are indicated by the dashed line, and area above the bolded line indicates stability of elemental sulfur.

Figure 4-5. Updated $E_{m}$-pH Diagram for the Cu-As-S system overlaid with CV Inflection Points.
4.10 References


Mikenda, W., Steidl, H., and Preisinger, A., 1982, “Raman Spectra of Na$_3$AsS$_4$$\cdot$8(D,H)$_2$O and Na$_3$SbS$_4$$\cdot$9(D,H)$_2$O and O-D(H)$\cdot\cdot\cdot$S Bonds in Salt Hydrates,” Journal of Raman Spectroscopy, 12(3), pp. 217-221.


5. Alkaline Sulfide Leaching

R.N. Gow¹, C Young¹, H Huang¹, G Hope²

¹Montana Tech of The University of Montana; 1300 W. Park; Butte, MT, 59701, USA
²Griffith University; 170 Kessels Road, Nathan, Qld, Australia, 4111

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5.1 Abstract

The reactivity of an enargite mineral electrode was investigated spectroelectrochemically under conditions typically found in alkaline sulfide leach solutions at pH 11-13 and Na₂S additions of 50 and 250 g L⁻¹. A bulk enargite electrode was cycled between 0 and -1000 mV for each set of solution conditions. Raman spectroscopy was used to determine and compare surface formations against species in mass-balanced Eₐ-pH diagrams generated using STABCAL. Previously, it was determined that arsenic could be selectively leached under alkaline conditions at an average solution potential of -300mV, across the pH range 11-13. Operating under such conditions allowed for selective leaching of arsenic with elemental sulfur formation. From several of the voltammograms obtained during this current testing, the formation of elemental sulfur appeared at increasingly reducing conditions with increasing sulfide concentration. At high concentrations, copper started to dissolve, possibly as a bisulfide complex, reducing the selectivity of the leach, unlike previous studies. However, the presence of the higher sulfide concentration is also anticipated to prevent passivation by consuming any surface formation of elemental sulfur. This study provides insight into the operating parameters of alkaline sulfide leaching in regards to the selectivity of arsenic leaching, as well as guidance for control of reagents and solution potential and, of course, the need for water treatment afterwards.
5.2 Introduction

Environmental limitations on pyrometallurgical processing of arsenic-bearing concentrates have forced operations to consider other solutions. Attempts to hydrometallurgically process enargite (Cu$_3$AsS$_4$) can be dual categorized: the co-dissolution of arsenic and copper under acidic conditions and the selective leaching of arsenic under basic conditions. The authors believe that the selective leaching of arsenic is more amenable because it produces a solid copper phase, preferably chalcocite (Cu$_2$S) or covellite (CuS) that could then be processed using conventional methods already in place in the copper and gold industries. Potential leaching methods include alkaline sulfide leaching (Achimovicova et al., 1999; Anderson and Twidwell, 2008a,b; Tongamp et al., 2009 and 2010), hypochlorite leaching (Vinals et al., 2003; Curreli et al., 2005; Mihaljovic et al., 2007), ammonia leaching (Gajam and Raghavan, 1983), and acid leaching (Gow et al., 2014b) with or without fine grinding to mechanically activate the enargite surface and increase normally slow leach reaction kinetics (Achimovicova et al., 1999; Balaz et al., 2000; Balaz and Achimovicova, 2006). In this study, the reactivity of enargite under alkaline sulfide leach conditions was examined.

Alkaline sulfide leaching has been shown to be a viable method in treating copper-ores containing high levels of arsenic and antimony, having been patented and used industrially at the operations of both the Sunshine Mine (Holmes and Coltrinari, 1973; Coltrinari, 1977; Anderson and Twidwell, 2008a,b) and Equity Silver Mine (Dayton, 1982). The process has also been shown to have potential for arsenic removal in colemanite processing (Delfini et al., 2003) and Waelz zinc oxide treatment (Li et al., 2011). Alkaline sulfide has the advantage of being selective for arsenic and antimony, under atmospheric conditions (~100°C) while producing a solid copper sulfide that can be processed more traditionally (Anderson and Twidwell, 2008a,b).
Arsenic and copper-arsenic sulfides such as orpiment (As$_2$S$_3$), enargite and tennantite (Cu$_{12}$As$_4$S$_{13}$) are solubilized as thioarsenite (AsS$_3^{3-}$) and thioarsenate (AsS$_4^{3-}$) according to Equations 1-3 (Filippou et al., 2007):

\[
\text{As}_2\text{S}_3 + 3 \text{ S}^2^- \rightarrow 2 \text{AsS}_3^{3-} \text{(aq)} \quad \text{Eq. 1}
\]

\[
2 \text{Cu}_3\text{AsS}_4 + 3 \text{ S}^2^- \rightarrow 3 \text{Cu}_2\text{S} (s) + 2 \text{AsS}_4^{3-} \text{(aq)} \quad \text{Eq. 2}
\]

\[
\text{Cu}_{12}\text{As}_4\text{S}_{13} + 10 \text{ S}^2^- \rightarrow 7 \text{Cu}_{1.714}\text{S} (s) + 4 \text{AsS}_4^{3-} \text{(aq)} \quad \text{Eq. 3}
\]

As indicated, orpiment completely solubilizes and, depending on the type of copper mineral being leached, either chalcocite (Cu$_2$S) or an anilite-like (Cu$_{1.714}$S) phase forms. However, it is understood that covellite (CuS) and other nonstoichiometric copper sulfides (Cu$_x$S) may form as well, depending on the redox chemistry of the system (Woods et al., 1987). The antimony sulfosalt series, stibnite (Sb$_2$S$_3$) and tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$) are known to behave relatively similarly (Awe and Sandstrom, 2010).

Several recent studies have shown that the kinetics of arsenic leaching improves by mechanical activation of concentrates (Achimovicova et al., 1999; Balaz et al., 2000; Balaz and Achimovicova, 2006). In this case, ultrafine comminution increases the surface area thereby enhancing the rate-determining surface reaction and yielding near-complete removal of arsenic within ten minutes of leaching as opposed to several hours. These studies also reported the formation of both solid and aqueous copper sulfide products, but were focused on how quickly the arsenic dissolved and not on identifying them.

Previous studies (Nadkarni and Kusik, 1988; Anderson and Twidwell, 2008a,b; Tongamp et al., 2010) have indicated the necessity of strict pH control when dealing with sulfide (S$^2-$) in order to limit the amount of hydrolysis and therefore the formation of bisulfide (HS$^-$) which appears to slow and even prevent further leaching. They argue that operating conditions must be
kept above pH 13, noting that these conditions are where sulfide ions predominate. However, it is noted that this transition brings to question the free energy of formation of the sulfide ion: 20.51 kcal/mol according to the National Bureau of Standards (NBS) (Wagman et al., 1982) database or 26.6 kcal/mol according to the MINTEQA2 (Allison et al., 1990) database used in this study. Using the MINTEQA2 value, bisulfide theoretically predominates up to pH 17 and various polysulfides (S$_x^{2-}$) species exist at slightly oxidizing conditions as shown in Figure 1. In accordance with the conclusion of the previous studies (Gow et al., 2014a,b), this $E_H$-pH diagram only considers sulfide oxidation to elemental sulfur thereby excluding the formation of all sulfoxyl species (e.g., thiosulfate, S$_2$O$_3^{2-}$; sulfite, SO$_3^{2-}$; and sulfate, SO$_4^{2-}$).

Contrary to these proposed reactions, a recent characterization of an alkaline sulfide leach residue (Torres, 2011) has indicated the formation of other copper sulfide species. Digenite (Cu$_9$S$_5$) and covellite were identified after six hours, while 97% of the arsenic was leached. Bornite (Cu$_5$FeS$_4$) was also identified due to the high pyrite content in the head sample. Further leaching, up to 24 hours, indicated near complete transformation of the solid species to a soluble sodium copper sulfide identified as NaCu$_5$S$_3$, perhaps the same undetermined species reported by Achimovicova (1999), Balaz (2000) and Balaz and Achimovicova (2006) by mechanical activation.

The discovery of a soluble copper sulfide phase is supported by the theoretical modelling put forth by Young (2003). Under conditions that would be found in an alkaline sulfide leach, copper is solubilized by excess bisulfide. The proposed copper thio-complexes are seen in the proposed $E_H$-pH diagram (see Figure 2). Covellite and chalcocite have the potential to be dissolved by excess bisulfide in solution. In this regard, there seems to be a conflict about
whether bisulfide enhances leaching or slows/stops the reaction as just mentioned (Nadkarni and Kusik, 1988; Anderson and Twidwell, 2008a,b; Tongamp et al., 2010).

In this study, spectroelectrochemical investigations using Raman spectroscopy and cyclic voltammetry on enargite under alkaline and acidic conditions (Gow et al., 2014a,b) are extended to alkaline sulfide leaching. The objectives are to increase the reactivity of enargite by improving the reaction kinetics or arsenic selectivity. This is accomplished by comparing Raman spectra and cyclic voltammetry scans over the pH range 11-13 at room temperature in the absence (Gow et al., 2014a) and presence of Na₂S.

![Figure 5-1. Eₜₐ-pH Diagram for S-H₂O System, (1M, 298K), using MINTEQ Thermodynamic Database and Assuming Oxidation to Elemental Sulfur Only, Ignoring all Sulfoxy Ions](image-url)
5.3 Thermodynamics

The free energy database used to calculate the mass-balanced diagrams for enargite (Gow et al., 2014a) was updated to include the soluble arsenic and copper thio-complexes (Young et al., 2000; Young et al., 2003). New mass-balanced $E_H$-$pH$ diagrams were calculated using STABCAL (Huang and Young, 1996; Huang, 2005; Huang et al., 2011) at $10^{-3}$, $10^{-5}$ and $10^{-7}$ M concentration values for copper and arsenic, in the presence of high sulfide concentrations of 50 and 250 g/L. The proposed diagrams are shown in Figures 3-6. Shaded areas predict regions of copper and arsenic dissolution. Selective arsenic leaching is shown to occur when the sulfur to copper molar ratio is at 640:1 (see Figures 3A and 4A). At or below this ratio, only arsenic should solubilize, leaving behind copper as either chalcocite or covellite. At higher ratios, the copper predominantly solubilizes as bisulfide complexes. Hence, as the sulfur content increases
relative to the amount of copper, the stability regions of covellite and chalcocite shrink. The remaining region of covellite stability, above -200mV, corresponds with the region of elemental sulfur formation determined in the previous alkaline reactivity testing (Gow et al., 2014a). Leaching must therefore be done at lower potentials. The region of thioarsenate (AsS$_4^{3-}$) stability is seemingly unchanged across the stability diagrams, suggesting that the Cu/S ratio is important to selectively leaching arsenic.
Figure 5-3. Mass-balanced $E_{\text{H}}$-pH Diagrams for the Cu-As-S system, 50 g L$^{-1}$ Na$_2$S for copper-bearing species. Shaded regions indicate where dissolution occurs.
A) 10-3 M Cu  B) 10-5 M Cu  C) 10-7 M Cu
Figure 5-4. Mass-balanced $E_\text{H}^\text{pH}$ Diagrams for the Cu-As-S system, 50 g L$^{-1}$ Na$_2$S for arsenic-bearing species. Shaded regions indicate where dissolution occurs.

A) $10^{-3}$ M As    B) $10^{-5}$ M As    C) $10^{-7}$ M As
Figure 5-5. Mass-balanced $E_{H}$-pH Diagrams for the Cu-As-S system, 250 g L$^{-1}$ Na$_2$S for copper-bearing species. Shaded regions indicate where dissolution occurs.

A) $10^{-3}$ M Cu  B) $10^{-5}$ M Cu  C) $10^{-7}$ M Cu
Figure 5-6. Mass-balanced $E_{\text{H}}$-pH Diagrams for the Cu-As-S system, 250 g L$^{-1}$ Na$_2$S for arsenic-bearing species. Shaded regions indicate where dissolution occurs.  
A) $10^{-3}$ M As  B) $10^{-5}$ M As  C) $10^{-7}$ M As
Table 5.1 - Standard Free Energy Values for Copper and Arsenic Thio-complexes
(Young et al., 2000; Young et al., 2003)

<table>
<thead>
<tr>
<th>Cu Species $^2$</th>
<th>$\Delta G^0$ (kcal)</th>
<th>As Species $^1$</th>
<th>$\Delta G^0$ (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(HS)$_2^-$</td>
<td>-5.68</td>
<td>AsS(OH)(HS)$^-$</td>
<td>-58.58</td>
</tr>
<tr>
<td>Cu$_2$S(HS)$_2^2$</td>
<td>-8.11</td>
<td>As(S(HS)$_2^-$</td>
<td>-9.08</td>
</tr>
<tr>
<td>CuHS$^0$</td>
<td>-2.85</td>
<td>As$_3$S$_2$(HS)$_2$</td>
<td>-25.33</td>
</tr>
<tr>
<td>Cu(HS)$_3^-$</td>
<td>-11.94</td>
<td>HAs$_3$S$_4$(HS)$_2$</td>
<td>-43.02</td>
</tr>
<tr>
<td>CuS(HS)$_3^+$</td>
<td>-0.85</td>
<td>As$_3$S$_4$(HS)$_2$</td>
<td>-33.22</td>
</tr>
</tbody>
</table>

5.4 Materials and Methods

Electrodes were created from enargite minerals obtained from mines in Butte, MT, USA and Quirivilca, Peru. Sections of the mineral were cut and shaped into approximate $\frac{1}{2}'' \times \frac{1}{2}''$ pieces and attached to copper wire using Electrodag 502 and carbon tape. They were placed into PTFE tubing and sealed with a non-conducting epoxy resin. Sample compositions were primarily enargite, with small amounts of silica and pyrite, as previously determined by X-ray Diffraction (XRD) and Scanning Electron Microscopy/Mineral Liberation Analysis (SEM/MLA) (Gow et al., 2014a,b). In-situ Raman Spectroscopy studies were conducted using a Renishaw Raman 100 InVia spectrophotometer. The system used a 100-mW He-Ne laser excitation source (632.8 nm) and was calibrated using the 520 cm$^{-1}$ primary band of pure silicon. Spectral manipulation was conducted using the GRAMS32 software. Details are presented in the previous publications (Gow et al., 2014a,b).

Buffer solutions were created for pH values 11 (sodium bicarbonate), 12 and 13 (potassium chloride), made according to the CRC Handbook (Haynes, 2011). Sodium sulfide (Na$_2$S) was added to each buffer solution yielding concentrations of either 50 or 250 g L$^{-1}$. 

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68 | P a g e
Sulfide concentration levels were identified from other similar studies (Nadkarni and Kusik, 1988; Awe and Sandstrom, 2010; Tongamp et al., 2009).

Further information was gathered using cyclic voltammetry. An electrochemical cell setup was combined with the Raman 100 to conduct multifile program studies. The 5-port cell had a transparent window and was fitted with Ag/AgCl saturated KCl reference (+0.197 vs SHE) and platinum counter electrodes. The multifile program was set up to take Raman spectra of the enargite electrode surface every ten seconds while the electrode was potentially cycled. The electrode was cycled negatively from 0 mV to -1000 mV vs SHE and back a total of three cycles.

5.5 Raman Spectroscopy

Raman spectroscopic profiling of the enargite electrode surface has been conducted in previous studies (Gow et al., 2014a,b). The characteristic peaks of potential surface formations were tabulated and reported there, and were used to determine potential surface formations during several static surface tests, where the solution potential was held constant for several minutes.

Chalcocite and covellite were the primary species identified during testing in agreement with the previous studies (Gow et al., 2014a,b). However, during tests with 250 g L\(^{-1}\) Na\(_2\)S solutions, a series of new peaks formed which were not identified. An example is shown in Figure 7 such that peaks at 445, 470, 985, 1000 and 1070 cm\(^{-1}\) were observed at -300 mV. Because these peaks were similar to the polysulfide peaks observed by Janz et al. (1976a,b,c), 50 mL of solution was collected from the electrochemical cell and evaporated using dry N\(_2\) gas. A Raman spectrum was taken of the resulting evaporate and, as also illustrated in Figure 7, the same peaks were observed although slightly shifted to 446, 495, 990, 1005 and 1070 cm\(^{-1}\). In
addition, a new peak appeared at 955 cm\(^{-1}\). Clearly, under these conditions, some copper is dissolving as predicted in Figures 5 and 6 for enargite at 250 g L\(^{-1}\).

Figure 5-7. Raman spectra of enargite (bottom) compared to enargite reacted at pH 12 and -300 mV with 250 g L\(^{-1}\) Na\(_2\)S (middle) and resulting evaporate crystallized out of solution (top)

At pH 12 and 250 g L\(^{-1}\) Na\(_2\)S, Figure 5 predicts that enargite will dissolve as CuS(HS)\(_3^{3-}\), Cu\(_2\)S(HS)\(_2^{2-}\) or Cu(HS)\(_3^{3-}\) and, when the potential is -300 mV, CuS(HS)\(_3^{3-}\) is expected to predominate. Upon evaporation, these species would crystallize out, perhaps as the copper sulfide identified as NaCu\(_5\)S\(_3\) by Torres (2011). Furthermore, based on the spectra obtained in previous studies (Gow et al., 2014a,b; Janz et al., 1976a,b,c), the unknown peaks are not characteristic of covellite or chalcocite. They also do not match the Raman spectra of nonstoichiometric copper sulfides found in the RRUFF database (Cu\(_{1.94}\)S – djurleite, Cu\(_{1.8}\)S – digenite, Cu\(_{1.78}\)S – roxbyite, Cu\(_{1.75}\)S – anilite, and Cu\(_{1.2}\)S – yarrowite).

In this regard, the solution conditions used by previous authors (Nadkarni and Kusik, 1988; Achimovicova et al, 1999; Curreli, 2009, Anderson and Twidwell, 2008a,b; Tongamp,
2009, Torres, 2011) are compiled in Table 2. Na$_2$S concentrations are close to those used to calculate the E$_H$-pH diagrams in Figures 3 and 4. Also included in Table 2 is the stoichiometry of the solid copper-sulfide that was produced in each study. Clearly, the stoichiometry of the copper sulfide span between that of chalcocite and covellite, Cu$_x$S (where 2 $\leq x \leq$ 1), and specifically yield values for “x” of 1, 1.4, 1.52, 1.8 and 2. Consequently, there does not seem to be a correlation between leaching conditions and the final product. Rather, it is likely a function of E$_H$, pH and possibly the presence of other minerals.

Table 5.2 - Leaching Conditions used by Previous Authors (adapted from Torres, 2011)

<table>
<thead>
<tr>
<th>Reference</th>
<th>% Cu</th>
<th>Na$_2$S (g L$^{-1}$)</th>
<th>Na$_2$S tested (g L$^{-1}$)</th>
<th>S/Cu Ratio Observed</th>
<th>NaOH conc. (g L$^{-1}$)</th>
<th>Copper Sulfide Product</th>
<th>Arsenic Leached (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Achimovicova, 1999</td>
<td>39</td>
<td>100</td>
<td>4</td>
<td>52</td>
<td>50</td>
<td>Cu$_{1.4}$S</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>Anderson and Twidwell (2008a,b)</td>
<td>18</td>
<td>100</td>
<td>250</td>
<td>2</td>
<td>20</td>
<td>-</td>
<td>99%</td>
</tr>
<tr>
<td>Curreli (2009)</td>
<td>33</td>
<td>33</td>
<td>10</td>
<td>8</td>
<td>100</td>
<td>Cu$_{1.52}$S, Cu$_2$S</td>
<td>98%</td>
</tr>
<tr>
<td>Gow et al. (this study)</td>
<td>44</td>
<td>250</td>
<td>electrode</td>
<td>---</td>
<td>pH 11-13</td>
<td>CuS, Cu$_2$S</td>
<td></td>
</tr>
<tr>
<td>Nadkarni and Kusik (1988)</td>
<td>25</td>
<td>160</td>
<td>363</td>
<td>2</td>
<td>1.5</td>
<td>Cu$_2$S</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Tongamp (2009)</td>
<td>33.7</td>
<td>200</td>
<td>100</td>
<td>5</td>
<td>50</td>
<td>Cu$_2$S</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Torres (2011)</td>
<td>32</td>
<td>80</td>
<td>50</td>
<td>4</td>
<td>100*</td>
<td>Cu$<em>2$S, Cu$</em>{1.8}$S, NaCu$_5$S$_3$</td>
<td>99%</td>
</tr>
</tbody>
</table>

5.6 Cyclic Voltammetry

Cyclic voltammograms (CV’s) determined in the presence of Na$_2$S were compared to those determined in its absence (Gow et al., 2014a). An example is shown in Figure 8 for results obtained at pH 13. Results suggest that reactions appear and/or shift to lower potentials with the increasing addition of Na$_2$S. It was determined that, in the absence of Na$_2$S, selective arsenic
dissolution occurred at an average potential of -300 mV over the pH range 11-13 according to the following oxidation reaction:

\[
\text{Cu}_3\text{AsS}_4 + 8 \text{OH}^- = 3 \text{CuS} + \text{S}^0 + \text{AsO}_4^{3-} + 4 \text{H}_2\text{O} + 5 e^- \quad \text{Eq. 4 (A1)}
\]

Elemental sulfur (S\(^0\)) appears even though it is not thermodynamically stable. However, its presence passivates the surface and thereby slows the reaction considerably as evidenced by the appearance of only one broad cathodic reaction. In this regard, peak C\(_1\) masks all of the other reactions which appear as shoulders, if at all. Because enargite is not stable under these alkaline conditions (Gow et al, 2014b), Reaction C\(_1\) is not the reverse of Reaction A\(_1\); rather, it is a series of reduction reactions involving the products as previously explained for the absence of Na\(_2\)S.

When Na\(_2\)S is added to the system, it equilibrates with bisulfide (HS\(^-\)) and reacts with elemental sulfur to form polysulfide (see Figure 1):

\[
\text{S}^{2-} + 2\text{OH}^- = \text{HS}^- + \text{H}_2\text{O} \quad \text{Eq. 5}
\]

\[
\text{yS}^0 + \text{HS}^- = \text{S}_{y+1}^{2-} + \text{H}^+ \quad \text{Eq. 6}
\]

where \(y = 1\) to 4. Thus, if elemental sulfur forms as with Reaction A\(_1\), it will be consumed and surface passivation will therefore be prevented. Figure 8 clearly shows that various cathodic reactions are unmasked and, furthermore, that current flow increases with increasing Na\(_2\)S addition, indicating that reaction rates are indeed enhanced.

Bisulfide will react with enargite, causing it to oxidize to covellite but, rather than forming arsenate (AsO\(_4^{3-}\)) as in Reaction A\(_1\), thioarsenate (AsS\(_4^{3-}\)) will form instead (see Figures 3 and 4):

\[
\text{Cu}_3\text{AsS}_4 + 3 \text{HS}^- + 3 \text{OH}^- = 3 \text{CuS} + \text{AsS}_4^{3-} + 3 \text{H}_2\text{O} + 3 e^- \quad \text{Eq. 7 (A2)}
\]
Reactions $A_1$ and $A_2$ explain how covellite can be observed in the absence and presence of Na$_2$S. Like Reaction $C_1$, the reverse reaction cannot occur because enargite is unstable under these conditions. Reaction $C_2$ therefore involves each of the products undergoing a series of reduction reactions.

![Cyclic Voltammograms of Enargite at pH 13](image)

**Figure 5-8.** Cyclic Voltammograms of Enargite at pH 13 in the presence of 250 g L$^{-1}$ Na$_2$S (top) and 50 g L$^{-1}$ Na$_2$S (middle) compared to its absence (bottom). See text for reaction details.

### 5.7 CuS Reduction

If bisulfide is present in significant amounts, it can lower the reducing potential of the solution and cause covellite to reduce to chalcocite and eventually metallic copper:

$$2\text{CuS} + \text{H}_2\text{O} + 2\text{e}^- = \text{Cu}_2\text{S} + \text{HS}^- + \text{OH}^- \quad \text{Eq. 8 (C}_2)$$

$$\text{Cu}_2\text{S} + \text{H}_2\text{O} + 2\text{e}^- = 2\text{Cu}^0 + \text{HS}^- + \text{OH}^- \quad \text{Eq. 9 (C}_3)$$

When covellite and chalcocite form and are exposed to excess bisulfide as well, they will solubilize:

$$\text{CuS} + 3\text{HS}^- = \text{CuS(HS)}_3^{3-} \quad \text{Eq. 10}$$

$$\text{Cu}_2\text{S} + 2\text{HS}^- = \text{Cu}_2\text{S(HS)}_2^{2-} \quad \text{Eq. 11}$$
Thus, by combining Reactions 8 and 10 as well as Reactions 9 and 11, the following reactions result, respectively:

\[ 3 \text{CuS} + 2 \text{HS}^- + \text{H}_2\text{O} + 2e^- = \text{Cu}_2\text{S} + \text{CuS(HS)}_3^{3-} + \text{OH}^- \quad \text{Eq. 12 (C}_{2a}\text{)} \]

\[ 2 \text{Cu}_2\text{S} + \text{HS}^- + \text{H}_2\text{O} + 2e^- = 2 \text{Cu}^0 + \text{Cu}_2\text{S(HS)}_2^{2-} + \text{OH}^- \quad \text{Eq. 13 (C}_{3b}\text{)} \]

It is expected that Reaction C\(_{2a}\) occurs at low sulfide addition (i.e., 50 g L\(^{-1}\)) and Reaction C\(_{3b}\) occurs at higher sulfide concentrations (i.e., 250 g L\(^{-1}\)). Both reactions explain the formation of the aqueous copper sulfide species observed in this study (see Figure 5) and other studies (Achimovicova et al., 1999; Balaz et al., 2000; Balaz and Achimovicova, 2006) but perhaps not necessarily yielding the exact NaCu\(_5\)S\(_3\) compound observed by Torres (2011).

As mentioned previously, it is understood that covellite may also reduce to form a series of nonstoichiometric copper sulfides before chalcocite is formed (Woods et al., 1987):

\[ x\text{CuS} + x\text{H}_2\text{O} + 2xe^- = \text{Cu}_x\text{S} + x\text{HS}^- + x\text{OH}^- \quad \text{Eq. 14} \]

where 2 \(\leq x \leq 1\). In this case, the nonstoichiometric copper sulfide will solubilize forming the same products in Reactions C\(_{2a}\) and C\(_{3b}\) but dependent on what “x” is:

\[ \text{Cu}_x\text{S} + a\text{HS}^- + b\text{H}_2\text{O} + c e^- = v \text{Cu}^0 + w\text{CuS(HS)}_3^{3-} + z\text{Cu}_2\text{S(HS)}_2^{2-} + b\text{OH}^- \quad \text{Eq. 15 (C}_4\text{)} \]

This is Reaction C\(_4\) and ultimately may account for the array of peaks that appear in Figure 6 as C\(_{4a-d}\) and A\(_{4a-d}\).

### 5.8 As\(_{S4}^{3-}\) Reduction

According to Figures 3 and 4, As\(_{S4}^{3-}\) may undergo two reduction reactions, first to HAsS\(_3^{2-}\) and then As\(^0\):

\[ \text{AsS}_4^{3-} + 2\text{H}_2\text{O} + 2e^- = \text{HAsS}_3^{2-} + \text{HS}^- + 2\text{OH}^- \quad \text{Eq. 16} \]

\[ \text{HAsS}_3^{2-} + 2\text{H}_2\text{O} + 3e^- = \text{As}^0 + 3\text{HS}^- + 2\text{OH}^- \quad \text{Eq. 17} \]
At high solution pH > 8, it is anticipated this occurs rapidly and the two equations may be combined such that:

\[
\text{AsS}_4^{3-} + 4 \text{H}_2\text{O} + 5 \text{e}^- = \text{As}^0 + 4\text{HS}^- + 4\text{OH}^- \quad \text{Eq. 18}
\]

Although As\(^0\) was not observed by Raman, its formation could be encompassed in the peaks and shoulders shown in Reactions C\(_{3a-b}\) and possibly masked by Reactions 8 and 13 which correspond to cathodic reactions C\(_5\) and C\(_{3b}\), respectively. These reactions yield Cu\(^0\) which occurs near the same potentials as As\(^0\) formation.

**5.9 Mass Balanced Diagrams**

Mass-balanced \(E_H - pH\) diagrams are presented in Figure 9A and B, overlaid for copper and arsenic containing species, considering 50 and 250 g L\(^{-1}\) Na\(_2\)S addition, respectively. Inflection points from the CV’s are plotted on them to see how thermodynamic predictions match experimental results. In some cases, there is good agreement. However, a majority of the disagreements appear to occur where nonstoichiometric species would be stable. These species were not considered in the STABCAL calculations for simplicity purposes but the problem also emanates from not knowing which species would form and its respective free energy data. Of course, reaction kinetics also play a role.
Figure 5-9. Mass-balanced $E_h$-$pH$ Diagrams for the Cu-As-S system; $3 \times 10^{-5}$ M Cu and $1 \times 10^{-5}$ M As; and S oxidation to sulfide only with A) 50 g L$^{-1}$ Na$_2$S and B) 250 g L$^{-1}$ Na$_2$S. The dotted line indicates the regions of water stability, arsenic-only transitions are indicated by the dashed line, and area above the bolded line indicates stability of elemental sulfur.
Conclusions

Results have shown that arsenic can be selectively leached but several factors need to be considered. The first involves controlling sulfide addition so that arsenic leaching is maximized and copper leaching is negligible, which appears to be related to the S:Cu molar ratio. Thermodynamic calculations suggest the sulfur to copper ratio should be 640:1 explaining why the Na$_2$S of 50 g L$^{-1}$ did not appear to cause Cu leaching whereas 250 g L$^{-1}$ did. The second involves controlling the E$_H$-pH conditions. Gow et al. (2014a) determined that, in the absence of Na$_2$S addition, selective alkaline leaching could be done between pH 11-13 and E$_H$ -600 to -300 mV. The results reported here have shown that arsenic solubility has been extended to a region between -800 to -300 mV. The upper range is similar due to elemental sulfur stability; however reactions with HS$^-$ and S$_2$O$_3^{2-}$ (Reaction 6) are anticipated to prevent surface passivation. The lower range decreased because the stability region of AsS$_4^{3-}$ was enhanced from -600 mV to -800 mV due to reaction with HAsS$_3^{2-}$ (Reaction 17). Furthermore, the pH range could theoretically be lowered to approximately pH 9. Enargite stability decreased from pH 11 to this value. The third involves treating the resulting alkaline sulfide solution to remove the arsenic and recycle the solution for further use.

The reactivity of an enargite mineral electrode was investigated spectroelectrochemically under conditions typically found during an alkaline sulfide leach, pH 11-13 and Na$_2$S additions of 50 and 250 g L$^{-1}$. A Raman spectrometer was used to determine and compare surface species against mass-balanced E$_H$-pH diagrams generated by STABCAL. Previously, it was determined that arsenic could be selectively leached at an average solution potential of -300 mV. Operating under these conditions allowed for selective leaching of arsenic and prevented elemental sulfur formation. From several of the CV’s obtained during the current testing, the formation of
elemental sulfur appears at more reducing conditions as the sulfide concentration increases. At a high enough concentration, copper starts to leach into solution, reducing the selectivity of the leach.

5.10 Acknowledgements

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5.11 References


R.N. Gow$^1$, H Huang$^2$, C Young$^2$

$^1$FLSmidth USA Inc., 7158 S FLSmidth Dr, Midvale, UT, 84047  
$^2$Montana Tech of the University of Montana; 1300 W. Park; Butte, MT, 59701, USA

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6.1 Abstract

$E_\text{H-pH}$ diagrams are useful tools in understanding how mineral surfaces react in solution and particularly how aqueous conditions can be changed to enhance mineral leaching processes. However, successful application of these diagrams requires several things be kept in mind to prevent what others have termed “gross errors” in their calculation and use. The aqueous Cu-S system is used as the basis for explaining the mass-balanced method of calculating $E_\text{H-pH}$ diagrams with the thermodynamic equilibrium software, STABCAL. The usage of Gibbs’ Phase Rule is employed in STABCAL to modify the diagrams and then applied to the aqueous Cu-As-S system. Resulting diagrams are compared against examples of those, generated using the predominant-ion method. The resulting mass-balanced diagram for enargite ($\text{Cu}_3\text{AsS}_4$) is noted to compare well with spectroelectrochemical measurements using Raman spectroscopy and cyclic voltammetry.
6.2 Introduction

Innovation into the processing of arsenic-bearing copper ores has been of particular interest. Copper arsenic sulfosalts minerals such as enargite (Cu₃AsS₄) and tennantite (Cu₁₂As₄S₁₃) are frequently prevalent in ore bodies as the oxide and easily leachable sulfides are harder to find. These minerals, unless pretreated somehow, concentrate in copper sulfide flotation processes, in turn concentrating the arsenic levels. Increasing environmental restrictions on arsenic content for smelters makes hydrometallurgical processing of these concentrates more favorable. While enargite is considered one of the more refractory copper sulfides, more so than chalcopyrite (CuFeS₂), there are still several methods, both industrially proven and in development, that are capable of processing these ore types. Alkaline sulfide leaching can be used as a pretreatment method to solubilize arsenic selectively (Delfini et al., 2003; Anderson and Twidwell, 2008; Tongamp et al., 2010a,b) or the entire metal content can be leached using acid-type leaches such as the acidified ferric sulfate (Dutrizac, 1981; Hackl et al., 1995; Klauber, 2008), chloride assisted, CESL (McDonald and Muir, 2007), or nitrogen species catalyzed (Anderson, 2003).

As these leaching technologies are developed, it is also important to develop an understanding of the mineral thermodynamics. To date, there are numerous studies on the Cu-Fe-S-H₂O system particularly as it relates to chalcopyrite leaching, yet very little on the Cu-As-S-H₂O system. Computer generated EₜₚH-pH diagrams have been employed to illustrate the importance of thermodynamic calculations in order to provide insight into such a system.

The thermodynamic equilibrium calculation software, STABCAL (Huang, 2013), is capable of diagrams based on the equilibrium line, or predominance ion, method and the point, or mass-balanced method. The predominant ion method was initially used by Garrels and Christ
(1965) and Pourbaix (1966) to produce diagrams for simple binary-metal water systems, such as Cu-H₂O. For simple binary systems, each method produces the same diagrams. Due to the lack of differences, it is not necessary to perform mass-balanced calculations. However, by increasing the number of components, as in the Cu-S-H₂O or Cu-As-S-H₂O systems, it becomes possible to have more than one phase present at any given Eₜ and pH, which is not apparent in a predominant ion diagram and, as termed by Robins (1993), can lead to "gross errors". The mass-balanced application of STABCAL has successfully been demonstrated for the Pb-S-H₂O, Cu-S-H₂O and Cu-Fe-S-H₂O systems (Huang and Young, 1996) and is now applied to the Cu-As-S-H₂O system.

However, in addition to the drawbacks of the predominance ion, other issues are noted throughout the literature that must be considered when using any such calculation software; primarily the use of consistent thermodynamic free energies (Linkson, 1996) and the consideration of metastable species in sulfur systems (Peters, 1986). These concerns are considered in more detail, along with validation of the final Eₜ-pH diagram through Raman spectroscopy and cyclic voltammetry.

6.3 Thermodynamic Data Inconsistencies

Linkson (1996) laid out several guidelines when dealing with computational programs for what he termed was the "blind-faith" culture. Most important was the data being used for the thermodynamic calculations. Data sources can be uncertain and unreliable, especially when combining data from various sources. STABCAL includes several databases (National Bureau of Standards (Wagman et al., 1982); MINTEQ2A (Allison et al., 1990); United States Geological Survey (Robie et al., 1974); National Institute of Standards and Technology Critical Database (Chase, 1998)) which can be used to keep the thermodynamic values internally consistent. When
combining databases for a comprehensive calculation, it is important to compare values and 
logically remove duplicates from them. For this reason, a personal database can be compiled and 
incorporated into the program to eliminate repetition if desired.

6.4 Metastable Considerations

The other issue indicated in literature dealing with such E<sub>H</sub>-pH diagrams is a need to 
differentiate between kinetics and equilibrium. Since thermodynamic calculations for such 
diagrams typically work on the basis of free energy minimization, they only return the most 
stable species given infinite time. Often, in order to get to this state, there must be a reaction path 
through one or multiple species that are only slightly less stable. Accounting for changes on an 
infinite time scale is not necessarily relevant to an industrial process. Consequently, metastable 
diagrams can be useful in understanding time scale and therefore reaction kinetics.

This is apparent in most sulfur containing systems. For example, elemental sulfur is 
resistant to oxidation unless solution conditions are aggressive. Most E<sub>H</sub>-pH diagrams for a 
sulfur containing system will include a large predominance range for sulfate; however, the sulfur 
regions do not account for a large energy barrier that exists in order to oxidize elemental sulfur to 
sulfate. Doing so extends the stability region of elemental sulfur as shown in Figure 1, by an 
estimated 300 kJ/mol (Peters, 1986) which “destabilizes” the sulfate. Forssberg (1984) made a 
similar statement by restricting the equilibrium constants of HSO<sub>4</sub>⁻ and SO<sub>4</sub>²⁻. Woods et al. 
(1987) used this concept for some of their E<sub>H</sub>-pH diagrams of chalcocite (Cu₂S) and similarly 
developed diagrams in their absence. Likewise, Gow et al. (2014a) determined E<sub>H</sub>-pH diagrams 
for the Cu-As-S-H₂O system and found it was more appropriate to limit the oxidation state of the 
sulfur-containing species to a maximum sulfur valence of zero, eliminating all sulfoxy species
including sulfate. Thus, oxidation to elemental sulfur only was considered thereby making their calculations more relevant.

Figure 6-1. $E_H$-$pH$ diagram for the S-H$_2$O system, indicating the extended sulfur stability region (Peters, 1986).

6.5 Mass Balanced $E_H$-$pH$ Diagrams

As noted, two primary methods exist to construct $E_H$-$pH$ diagrams. The first method, known as the equilibrium line or predominance ion method, is used to construct boundary lines between two adjacent species based on a given equilibrium activity or concentration. If ligand components are involved, the domains from the ligand species are first determined before the species from the component can be plotted (Garrels and Christ, 1989; Huang 2013).
The second method, the mass-balanced method (Forssberg et al., 1984; Huang, 2013), performs equilibrium calculations by considering all species from all components at the same time for each point on the \( E_H - \text{pH} \) diagram. Huang (2005) explains that the STABCAL program does this by forcing mass-balance constraints onto the equilibrium constants. With STABCAL, the number of points considered for each diagram is referred to as the resolution. It is typically set at 800x385 as used for each diagram generated in this study. In this regard, the pH range is split into 800 lines, for which there are 385 \( E_H \) points to calculate. In this regard, the entire diagram is composed of 308,000 individual calculations. This number can be increased or decreased as needed. Up to a maximum of \( 1 \times 10^6 \) calculations are allowed. Once equilibrium concentrations are calculated at a given point, the resulting component is recorded. Boundary lines are then drawn between two different species. Depending on the usage of the diagram, several different diagrams can be plotted, shown in the following examples.

To simplify the following illustration, the \( E_H - \text{pH} \) of copper complexed with sulfur and water is used. Species and thermodynamic data are taken from the same database as from the Cu-As-S-H\(_2\)O system mentioned earlier. Ionic strength of the solution is assumed to be zero and the equilibrium concentrations of aqueous Cu and S are set at 1.0E-2 mole/L. An equilibrium \( E_H - \text{pH} \) diagram calculated by STABCAL for the Cu-S-H\(_2\)O system at 1.0E-2 mole/L using the line method is shown in Figure 2. Each area is occupied by only one species. If the concentration of Cu is decreased to 1.0E-5 mole/L, the diagram changes slightly as represented by blue lines and species overlaid on the diagram. When such a low concentration of Cu is used, the domain for aqueous CuSO\(_4\) increases extending to higher pH and lower \( E_H \) and consuming the regions previously occupied by solids.
By comparison, the $E_H$-pH diagrams shown in Figures 3 and 4 were also calculated with STABCAL but with mass-balance constraints assuming a total mass of Cu and S to be 0.01 mole/L and using a resolution of 800x385. The mass-balanced diagram in Figure 3 reveals the same solids being stable but also indicates many solids are co-stable with another solid: $\text{Cu}_2\text{S}+\text{CuS}$, $\text{Cu}_2\text{S}+\text{Cu}$, and $\text{Cu}_4\text{SO}_4(\text{OH})_6+\text{CuO}$, and $\text{Cu}_4\text{SO}_4(\text{OH})_6+\text{Cu}_2\text{O}$. It should be noted that the diagram is plotted for copper-containing species; for simplicity purposes, stable sulfur-only species are not plotted. Figure 4 results when only the predominant solid of the co-stable regions is considered. Figure 4 is similar to Figure 2 with the exception that CuS stability region is slightly smaller and the equilibrium between $\text{Cu}^{2+}$ and $\text{CuSO}_4$ is shifted to a higher pH.

![Figure 6-2. $E_H$-pH diagram of Cu-S-H$_2$O system constructed by the equilibrium line method. 25 °C, 1 atm. Equilibrium concentration of [S] = [Cu] = 1.0E-2 moles/L. Sulfur oxidation to sulfate. Cu-containing species only. Overlaid blues lines represent [S] = [Cu] = 1.0E-5 moles/L.](image-url)
Figure 6-3. Cu-S-H$_2$O mass-balanced $E_{H^+}$-pH diagram showing multiple co-stable regions of solids. Conditions are same as Figure 1. Labels 1 to 3 are locations that are discussed later in this paper.

Figure 6-4. Cu-S-H$_2$O mass-balanced $E_{H^+}$-pH diagram with predominant aqueous and solid species. Conditions are the same as Figures 2 and 3.
6.6 Equilibrium Calculation and Gibbs’ Phase Rule for Mass-balanced E<sub>H</sub>-pH Diagram

Different from free energy minimization methods used in, for example, SOLGASWATER (Eriksson, 1979); STABCAL utilizes the law of mass action by combining equilibrium constants with mass inputs for solving equilibrium concentrations. The stable solids have to be searched and their equilibrium equations incorporated in the calculation. Searching for stable solids is made easier using aids such as saturation indices (SI) and Gibbs’ phase rule (Huang and Young, 1996). The mass action calculation process is illustrated for Cu-S-H<sub>2</sub>O system by picking point 1 from Figure 3: E<sub>H</sub> = 0.1V and pH = 2. Again, for simplicity and clarity, the ionic strength is assumed to be zero.

6.7 System Components – Master and Non-master Species

All E<sub>H</sub>-pH diagram calculations include H<sub>2</sub>O and therefore have three mandatory components: H<sup>+</sup>, O<sup>2-</sup> and e<sup>-</sup>. Additional components must be added to the system to include other elements. Depending on the thermodynamic database(s) being used, various species involving only O, H and those elements are considered. Finally, to enable the mass-balanced calculation, a “master species” for each additional element is selected, sometimes arbitrarily. These are usually aqueous species and allow the equilibrium mass-balance expressions to be solved more easily. The concentrations of all “non-master species” are determined afterwards. As an example, for the Cu-S-H<sub>2</sub>O system, Table 2 lists the five components that need to be considered along with the master species being used as well as the number of non-master species. In this case, Cu<sup>2+</sup> and H<sub>2</sub>S(aq) were chosen as the master species and the NBS database (Wagman et al., 1982) was used, yielding 53 other species of which 19 contained only S and 34 contained Cu with or without S.
Table 6.1 - Components, master and non-master species for calculating an $E_{\text{H}}$-pH diagram for the Cu-S-H$_2$O system using the mass action method.

<table>
<thead>
<tr>
<th>Component</th>
<th>Master Species</th>
<th># of Species</th>
<th>Types of reaction and species involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>H$^+$</td>
<td>None</td>
<td>Protonation and De-protonation</td>
</tr>
<tr>
<td>e$^-$</td>
<td>e$^-$</td>
<td>None</td>
<td>Oxidation and Reduction</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>H$_2$O</td>
<td>1</td>
<td>Hydration and De-hydration</td>
</tr>
<tr>
<td>S$^{0}$</td>
<td>H$_2$S (aq)</td>
<td>19 S only</td>
<td>All S and CuS for mass balance of S</td>
</tr>
<tr>
<td>Cu$^0$</td>
<td>Cu$^{2+}$</td>
<td>34 Cu + Cu-S</td>
<td>All Cu and CuS for mass balance of Cu</td>
</tr>
</tbody>
</table>

Concentrations of the aqueous species from the non-master species can be expressed in terms of the activities from the master species and their equilibrium constants. For instance, CuSO$_4$ yields the following equilibrium equation and concentration quotient:

$$\text{Cu}^{2+} + 4\text{H}_2\text{O} + \text{H}_2\text{S} = 8\text{e}^- + \text{CuSO}_4(\text{s}) + 10\text{H}^+ \quad [\text{Eq. 3}]$$

$$K = 10^{-38.31999668} = \frac{[\text{e}^-]^8[\text{CuSO}_4][\text{H}^+]^{10}}{[\text{Cu}^{2+}][\text{H}_2\text{S}]} \quad [\text{Eq. 4}]$$

Since ionic strength of zero is assumed for the solution, the equilibrium quotient is expressed in terms of concentration as [species]. Unit activity is used for all solids, liquids and H$_2$O. The activity of gaseous components is in atmospheric pressure. Because of unit activity, the reaction quotient for a solid species is different from the quotient of an aqueous species as shown by, for example, solid CuS:

$$\text{Cu}^{2+} + 2\text{e}^- + \text{H}_2\text{S} = \text{CuS}(\text{s}) + 2\text{H}^+ \quad [\text{Eq. 5}]$$

$$K = 10^{33.6690846} = \frac{[\text{H}^+]^2}{[\text{Cu}^{2+}][\text{e}^-]^2[\text{H}_2\text{S}]} \quad [\text{Eq. 6}]$$

Saturation indices (SI) are commonly used to check for the presence of a solid and are calculated by the difference $\log K - \log Q$ where $Q$ is the equilibrium quotient. A positive SI means the solid is oversaturated and will be present. A negative SI indicates that the solid is unsaturated and will not be present. If it is zero, the solid is in equilibrium with the solution. STABCAL
defines the equilibrium equation as the formation of solid (precipitation) rather than its ionization (dissolution) as used by other modeling programs such as MINTEQA2.

For the Cu-S-H₂O system using NBS data, there are 39 aqueous species whose equilibrium concentrations need to be calculated, requiring 39 different linear and non-linear equations to solve, including 34 equilibrium equations from the non-master species. One species each from the given Eₚ and pH, one each from the given Cu and S mass inputs, and one from the unit activity of H₂O (at no ionic strength). STABCAL solves these equations using the Newton-Raphson iterative method.

Table 3 shows the results of a calculation for the Cu-S-H₂O system at pH 2 and Eₚ 0.1V (i.e., Point #1 in Figure 3) and includes equilibrium concentrations for the five master species and two of the non-master species (i.e., CuSO₄(aq) and Cu⁺), along with the SI of eight solids. Because each SI is positive, each solid is oversaturated and therefore seemingly stable (i.e., precipitated). It therefore becomes necessary to identify the exact solids that are stable, reject the non-stable solids, and re-calculate the equilibrium concentrations of all involved species. Hence, a trial-and-error search method is used to find the stable solids with the help of both the SI values and Gibbs’ phase rule (see discussion in the next section). The search is repeated until the SI of each precipitated solids becomes zero, and is less than zero for unsaturated solids. Table 4 shows the results when the calculation is completed. A comparison to Table 3 shows that the concentrations of the two master species and the two example non-master species have changed, Likewise, six of the solids had SI values become negative and therefore do not precipitate; however, the other two solids, CuS and Cu₂S, have SI values of zero and are therefore stable and precipitate. CuS is noted to predominate (compare Point #1 in Figure 3 and 4).
Table 6.2 - STABCAL initial calculation for Cu-S-H$_2$O system at pH = 2 and E$_H$ = 0.1V.

<table>
<thead>
<tr>
<th>Master Species</th>
<th>Conc (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>2.04E-02</td>
</tr>
<tr>
<td>H$^+$</td>
<td>1.00E-02</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>9.98E-03</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>9.09E-04</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Non-Master Aqueous</th>
<th>Log K</th>
<th>Conc (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO$_4$</td>
<td>-38.32</td>
<td>1.45E-10</td>
</tr>
<tr>
<td>Cu$^+$</td>
<td>2.69</td>
<td>9.09E-03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solid Species</th>
<th>Log K</th>
<th>SI</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>-4.90</td>
<td>0.48</td>
</tr>
<tr>
<td>Cu</td>
<td>11.47</td>
<td>5.05</td>
</tr>
<tr>
<td>CuS</td>
<td>15.73</td>
<td>14.68</td>
</tr>
<tr>
<td>Cu$_{1.75}$S</td>
<td>28.93</td>
<td>23.07</td>
</tr>
<tr>
<td>Cu$_{1.8}$S</td>
<td>29.47</td>
<td>23.29</td>
</tr>
<tr>
<td>Cu$_{1.95}$S</td>
<td>32.22</td>
<td>25.08</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>7.30</td>
<td>1.83</td>
</tr>
<tr>
<td>Cu$_2$S</td>
<td>33.67</td>
<td>26.20</td>
</tr>
</tbody>
</table>

Table 6.3 - STABCAL equilibrium calculation for Cu-S-H$_2$O system at pH = 2 and E$_H$ = 0.1V.

<table>
<thead>
<tr>
<th>Master Species</th>
<th>Conc (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>2.04E-02</td>
</tr>
<tr>
<td>H$^+$</td>
<td>1.00E-02</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>6.89E-06</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>2.73E-15</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Non-Master Aqueous</th>
<th>Log K</th>
<th>Conc (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO$_4$</td>
<td>-38.32</td>
<td>3.00E-25</td>
</tr>
<tr>
<td>Cu$^+$</td>
<td>2.69</td>
<td>2.73E-14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solid Species</th>
<th>Log K</th>
<th>Conc (M)</th>
<th>SI after precip</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>-4.90</td>
<td>0</td>
<td>-2.7</td>
</tr>
<tr>
<td>Cu</td>
<td>11.47</td>
<td>0</td>
<td>-6.5</td>
</tr>
<tr>
<td>CuS</td>
<td>15.73</td>
<td>9.99E-03</td>
<td>0.0</td>
</tr>
<tr>
<td>Cu$_{1.75}$S</td>
<td>28.93</td>
<td>0</td>
<td>-0.3</td>
</tr>
<tr>
<td>Cu$_{1.8}$S</td>
<td>29.47</td>
<td>0</td>
<td>-0.6</td>
</tr>
<tr>
<td>Cu$_{1.95}$S</td>
<td>32.22</td>
<td>0</td>
<td>-0.6</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>7.30</td>
<td>0</td>
<td>-21.2</td>
</tr>
<tr>
<td>Cu$_2$S</td>
<td>33.67</td>
<td>6.89E-06</td>
<td>0.0</td>
</tr>
</tbody>
</table>
6.8 Gibbs’ Phase Rule for E$_{\text{H}}$-pH Mass-action Calculation

Gibbs’ Phase Rule, also known simply as The Phase Rule, can be used to determine the potential number of phases under particular conditions in the system. It is more typically applied by geologists, pyrometallurgists and ceramicists to temperature-pressure as well as binary, ternary and quaternary diagrams. The equilibrium calculation for an aqueous system, including mass-balanced E$_{\text{H}}$-pH calculations, should comply; otherwise, correct calculations may not be obtained. However, to apply this rule to E$_{\text{H}}$-pH and other aqueous diagrams, several facts need to be illustrated. Aqueous systems have three built-in components which are not normally mentioned or even shown on corresponding diagrams: H$^+$, O$^{2-}$ and e$^-$. Water, which encompasses all dissolved species, must be considered a phase in addition to all solids and gasses as well as other liquids. Each elemental component considered allows an additional solid, liquid or gas to be considered as originally noted by Gibbs (1875, 1878):

$$P = C - F + 2$$  \[\text{Eq. 7}\]

where the number of phases, $P$, is determined by the number of components, $C$, minus the degrees of freedom, $F$, plus two to encompass the variables, temperature and pressure. Temperature must be fixed for every particular E$_{\text{H}}$-pH diagram, as the free energy values used are typically determined for 25°C. If the system involves no gaseous species, the pressure is normally assumed equal to 1 atm. If gaseous species are considered, the pressure is no longer predetermined; rather, an additional phase must be considered. The total number of phases in an aqueous system is therefore comprised of water, gas and one solid from each component:

$$P_{\text{total}} = 1_{\text{water}} + n_{\text{elements}} + 1_{\text{gas}}$$  \[\text{Eq. 8}\]

The maximum number of solid species is then:

$$P_{\text{maximum}} = C - F - 1$$  \[\text{Eq. 9}\]
For the Cu-S-H$_2$O system, $C = 5$ since there are five components: $H^+$, $O^2-$, $e^-$, Cu and S. Thus, $P_{\text{maximum}} = 4 - F$ and, at any given point on an $E_H$-pH diagram, $F = 2$ and $P_{\text{maximum}} = 2$. Figure 3 which, as already noted, showed there were several areas where solids were co-stable: $Cu_2S+CuS$, $Cu_2S+Cu$, and $Cu_4SO_4(OH)_6+CuO$, and $Cu_4SO_4(OH)_6+Cu_2O$. Likewise, for boundaries and triple points with these co-stable solids, $F = 1$ and $P_{\text{maximum}} = 3$. Only one point occurred in Figure 3, and is labeled Point #3 with the adjacent solids being $Cu_4SO_4(OH)_6+CuO+Cu_2O$. An enlarged view of this region is shown in Figure 5 where a boundary is observed between two triple points. It is further noted that no conditions exist where $F = 0$ and $P_{\text{maximum}} = 4$.

When the amount of S is increased from 1.0E-$2$ to 1.5E-$2$ moles/L, while the amount of Cu is kept the same, the mass-balanced $E_H$-pH diagram shown in Figure 6 is the result. Comparing Figures 3 and 6 indicates there are several differences. For example, the co-stability region of $Cu_2S+CuS$ all but disappears because the increased S causes $Cu_2S$ to become unstable, effectively leaving $CuS$ as the only stable Cu-solid. However, within the $CuS$ region and in place of the $Cu_2S$ that disappeared, elemental sulfur precipitates. Even under these conditions, the Gibbs’ Phase Rule must still be satisfied. It can be seen that in order for elemental sulfur to become stable within the small region noted in Figure 6, the stability of $Cu_2S$ must decrease and convert to $CuS$. The three together are not able to coexist since it would violate the maximum number of solids for $F=2$.

The other major change that is shown is a shift in the equilibrium of the cupric ion as the increased S increases the sulfate in solution and expands the region of aqueous copper sulfate. The oxygen-containing copper species are unaffected by the increase in sulfur content, and the majority of the diagram remains unchanged.
Figure 6-5. Enlarged Cu-S-H₂O mass-balanced Eₘₜₐₜ-pH diagram showing boundary between the 2 co-stable regions. Conditions are the same as Figures 2-4.

Figure 6-6. Cu-S-H₂O mass-balanced Eₘₜₐₜ-pH diagram, [S] = 1.5E-2 moles/L. All other conditions are same as Figures 2-5.
6.9 Cu-As-S-H₂O (Enargite) Thermodynamics

There have been previous thermodynamic diagrams (Padilla et. al, 2008) for the Cu-As-S-H₂O system developed for enargite. The example diagram, (see Figure 7) essentially overlays the various binary diagrams (Cu-H₂O, S-H₂O and As-H₂O) to identify the region of enargite stability. Because this approach is similar to the equilibrium line-method for calculating E_H-pH diagrams, it is only accurate for binary systems and not ternary and above. It also ignores other Cu-As-S interactions by not considering the potential formation of the solids listed earlier in Table 1 and is therefore regarded to be incomplete. Mass-balanced calculations are not only beneficial, Gibbs’ Phase Rule necessitates it due to the fact that Cu-As-S-H₂O system is a quaternary system such that, according to Equation 5, \( P_{\text{maximum}} = 3 \) with \( C = 6 \) (H⁺, O²⁻, e⁻, Cu, As and S) and \( F = 2 \) (E_H and pH). As will be concluded herein, mass-balanced calculations can make a complex system become simple.

To contrast this predominance diagram, in regards to the need for a more comprehensive thermodynamic database, the same diagram was generated using STABCAL (see Figure 8). Three diagrams were calculated to plot the Cu-, As- and S-containing predominant species. The diagrams are overlaid using STABCAL and then edited using drawing software. Because this complex of a system is typically not shown, some explanation of the diagram is necessary to aid its comprehension. The parallel dotted lines, which are common to E_H-pH diagrams, are the water stability lines. Bolded lines are used to indicate sulfur transition boundaries while dashed lines indicated arsenic-only transition boundaries. For instance, the predominant arsenic-containing species transitions from \( \text{Cu}_2\text{AsO}_4\text{OH} \) to \( \text{HAsO}_4^{3-} \) along the sloped dashed line between pH 8 and 9; however, \( \text{Cu}_2\text{AsO}_4\text{OH} \) is still the primary copper-containing species until the vertical, unbroken boundary line at approximately pH 8.5.
Duplicate labels are added as needed for clarity and finally, aqueous species are differentiated from solid species with italicized labels. The diagram in Figure 8 was generated using activities/concentrations similar to, but slightly different from that of Figure 7. The concentration ratios are modified to mimic that of enargite (0.075:0.025:0.1).

The first notable difference between the mass-balanced diagram, Fig. 8, and that in Fig. 7 is the interaction of copper and arsenic in regions other than that of enargite. The inclusion of other copper-arsenic sulfosalt results in small regions of their stability. The size and occurrence of their stability is shown to be very dependent on the concentrations of copper, arsenic and sulfur used due to mass-balance constraints, similar to the differences noted between Figures 3 and 6 earlier, and discussed in further detail by Gow et. al., 2014d.
Other interactions between arsenic and sulfur, known as thioarsenates, occur above pH 11, under reducing conditions. These are the basis of alkaline sulfide leaching. There are also subtle differences in the size and shape for various other species, particularly $H_2S$ and $HS^-$ as they interact with copper and transition to $Cu_2S$. However, these diagrams can be produced for any number of conditions desired but require some amount of knowledge of the system to justify the final result.

With that in mind, a mass-balanced $E_H$-$pH$ diagram, updated from previous enargite studies is proposed and compared against the previously described diagrams (see Figure 9). The database for this diagram has been slightly altered to corroborate the data obtained from Raman spectroscopy. Copper oxides $CuO$ and $Cu_2O$ were removed from consideration and sulfide oxidation was limited elemental sulfur. The diagram scheme is similar to that in Fig. 8.

The removal of sulfoxy species allows enargite and the copper-arсенic sulfosalt stability to expand, into more oxidizing conditions. Copper, $CuO$ and $Cu_2O$ are replaced by $CuS$ which was not previously seen in Figure 8 and elemental sulfur is now stable across the entire pH range.

6.10 Validation of $E_H$-$pH$ Diagrams

The final check on the diagrams, in order to minimize errors discussed by Peters (1986), Robins (1993) and Linkson (1996), and to validate the results, was to use Raman spectroscopy in conjunction with cyclic voltammetry to study the surface transformations of an enargite electrode under various solution pH and potential conditions. The results from these studies (Gow et al., 2014a, b) were used to identify formations and the region of conditions where they occurred. These regions were then compared with diagrams produced by STABCAL and species were removed as necessary. The final diagrams were reported and compared well with the mass-balanced $E_H$-$pH$ diagrams that were generated.
Figure 6-8. Complete $E_{\text{H}}$-pH Diagram for the Cu-As-S system, $[\text{Cu}]=7.5\times10^{-2}$M, $[\text{As}]=2.5\times10^{-2}$M, $[\text{S}]=1.0\times10^{-1}$M. Sulfur oxidation includes all sulfoxyl species.
Figure 6-9. Complete Updated $E_h$-pH Diagram for the Cu-As-S system, $[\text{Cu}]=7.5\times10^{-2}\text{M}$, $[\text{As}]=2.5\times10^{-2}\text{M}$, $[\text{S}]=1.0\times10^{-1}\text{M}$. Sulfur oxidation is limited to elemental sulfur.
6.11 Conclusions

Predominance-ion and mass-balanced \(E_H-pH\) diagrams for the Cu-As-S-H\(_2\)O system were generated using STABCAL, a thermodynamic stability calculation program. The predominance-ion method can accurately portray binary systems, as indicated by the phase rule, where only one phase is possible in regions of predominance. However, as the number of components increases, such as in ternary and quaternary aqueous systems, the number of phases that are possibly at any given point in a diagram increases, as dictated by Gibbs’ Phase Rule. Applying predominance diagrams to these systems is much more difficult. It is necessary to include mass-balance constraints and ligand competition that more accurately describe the system. New mass-balanced \(E_H-pH\) diagrams were generated for the Cu-As-S-H\(_2\)O system and compared against the predominance method to determine the primary differences.

Two different databases of thermodynamic data were used to generate the mass-balanced diagrams. The first considered all of the species that were compiled for this study while the second limited the sulfur oxidation to elemental sulfur. All sulfoxy containing species were removed to account for the kinetic limitations of elemental sulfur formation. The surface of an enargite mineral was studied with Raman spectroscopy and cyclic voltammetry, as aqueous conditions were changed, to identify surface formations. The resulting data indicated that the limited database more appropriately modelled the reactivity of the enargite surface and validated the mass-balance method employed by STABCAL.

In this regard, STABCAL is capable of rapidly generating mass-balanced \(E_H-pH\) diagrams that can accurately model difficult ternary and quaternary aqueous systems. This method limits the "gross errors" of the predominance-ion method identified by other authors.
6.12 References


7. Utility of Mass-Balanced E$_{H}$-pH Diagrams II: Stoichiometry of Cu-As-S-H$_2$O System
R.N. Gow$^1$, H. Huang$^2$, C. Young$^2$

$^1$FLSmidth USA Inc., 7158 S FLSmidth Dr, Midvale, UT, 84047
$^2$Montana Tech of The University of Montana; 1300 W. Park; Butte, MT, 59701, USA

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7.1 Abstract

Previously, Gibbs’ phase rule was applied to mass-balanced E$_{H}$-pH diagrams for the Cu-As-S-H$_2$O system. Diagrams were generated using the stoichiometry of enargite as a basis. In this study, the calculations were expanded to cover the stoichiometries of three other Cu-As-S minerals (tennantite, sinnerite, and lautite) and compared to enargite. Stability regions within the resulting E$_{H}$-pH diagrams were found to change with stoichiometry such that a particular mineral would predominate if its stoichiometry was used in the calculation. Solution speciation was also found to vary, with thioarsenate being the best example. This stoichiometric effect helps to explain results reported in the literature and would be difficult to realize if it were not for mass-balanced calculations.
7.2 Introduction

A comprehensive thermodynamic review has recently been conducted on the aqueous copper-arsenic-sulfur system (Gow et al., 2014a-d). The free energies of over 100 species were collected from various authors and thermodynamic databases to produce mass-balanced $E_\text{H}_2\text{O}$-pH diagrams, using the thermodynamic equilibrium calculation software, STABCAL (Huang, 2014). The full database was listed and discussed by Gow et al. (2014a). Resulting diagrams were generated for enargite and confirmed with Raman spectroscopy using bulk mineral electrodes in order to identify reactions spectroelectrochemically. Theoretical calculations agreed well with the experimental results under alkaline conditions (Gow et al., 2014a), acid conditions (Gow et al., 2014b), and alkaline sulfide leaching conditions (Gow et al., 2014c).

In this study, additional mass-balanced $E_\text{H}_2\text{O}$-pH diagrams are generated by changing the copper-arsenic-sulfur stoichiometry from enargite ($\text{Cu}_3\text{AsS}_4$) to tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), sinnerite ($\text{Cu}_6\text{As}_4\text{S}_9$) and lautite ($\text{CuAsS}$). Regions for the thermodynamically stable species are shown to change with the four different mineral compositions. Potential leach conditions, both for co-dissolution and selective dissolution techniques, were examined for differences in predominant species according to changing copper-to-arsenic ratios, sulfur compositions, and sulfur oxidation states.

7.3 Experimental

STABCAL was used to produce $E_\text{H}_2\text{O}$-pH diagrams for the Cu-As-S-$\text{H}_2\text{O}$ system with stoichiometries corresponding to each of the copper arsenic sulfosalt minerals listed in Table 1. Although it is unfortunate that a free energy for lautite is not available, results will show that it not that critical to the discussions. Each diagram was produced using the mass-balanced method as opposed to the predominant ion method. Diagrams, initially created using the predominant-ion
method were determined to not be accurate enough to describe a quaternary system, such as Cu-As-S-H₂O (Robins, 1993). Typically, the mass-balanced calculations provide more accurate E_H-pH diagrams for anything more complex than a binary metal-water system. The validation of the mass-balanced method and the errors associated with trying to apply the predominant ion to such a complicated diagram have been discussed (Gow et al., 2014d) and are elaborated herein.

**Table 7.1 - Free Energy Values for Cu-As-S Species not found in the MINTEQ2A/USGS Databases**

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔG (kcal)</th>
<th>Species</th>
<th>ΔG (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₃AsS₄ Enargite [Craig]</td>
<td>-49.808</td>
<td>Cu(AsO₂)₂ [Nishimura]</td>
<td>-169.2</td>
</tr>
<tr>
<td>Cu₁₂As₄S₁₃ Tennantite</td>
<td>-180.908</td>
<td>Cu₃As Domeykite [Barin]</td>
<td>-3.184</td>
</tr>
<tr>
<td>Cu₆As₄S₉ Sinnerite [Craig]</td>
<td>-110.256</td>
<td>H₃AsSO₂ [Helz]</td>
<td>-103.412</td>
</tr>
</tbody>
</table>

Gow et al. (2014a) compiled a comprehensive thermodynamic database of the Cu-As-S-H₂O system primarily from the MINTEQ2A database (Allison, 1991) which lists values in the form of Log K. However, for use in STABCAL, they were converted to free energy, ΔG. The database was then predominantly supplemented with values from the US Geological Survey database (Robie, 1984). Free energy values for various solids, particularly the solid Cu-As sulfosalts, were taken from other references (see Table 1). To illustrate, the thermodynamic values for several of the more commonly found copper arsenic sulfosalts were compiled from Craig and Barton (1973). Inclusion of these free energy values with the MINTEQ2A database creates some amount of error; however, these values are the only such available for the Cu-As-S minerals. Craig and Barton (1973) list five such minerals: luzonite and enargite (Cu₃AsS₄), which are polymorphs, tennantite (Cu₁₂As₄S₁₃), sinnerite (Cu₆As₄S₉), and an unnamed formation, Cu₂₁As₁₂S₃₁. The full database was then made consistent and used herein and elsewhere (Gow et al., 2014a-d).
7.4 Diagram Generation and Overlay

The compiled thermodynamic database and the standard free energies of the copper-arsenic sulfosalts have been used to generate mass-balanced $E_H$-pH diagrams for the Cu-As-S-H$_2$O system. Each diagram for this study was generated at 25°C, with a resolution of 800 x 385. Higher resolutions, up to 1200 x 800, can be used if boundary lines need to be better defined, requiring almost 1 million calculations points, which can be time consuming depending on the specifications of the computer being used. As computer processors become increasingly powerful, the length of time decreases and currently takes about 15-30 minutes per diagram. A more in-depth explanation of the STABCAL program can be found in Huang (2014).

Using the conditions mentioned above and the stoichiometries of each copper-arsenic sulfosalt, mass-balanced $E_H$-pH diagrams for each component of copper, arsenic and sulfur were determined using STABCAL and then overlaid to yield the final diagram. Examples of the component diagrams for the tennantite system, with sulfur oxidation limited to elemental sulfur, are shown in Figure 1A-C. Each diagram is then used to produce the final overlay shown in Figure 2. To do this, boundary lines from the arsenic and sulfur diagrams shown in Figure 1B & C were added to the copper diagram in Figure 1A, but only if they were not already common to one another.

Due to the complexity of the system, and the number of species that appear in order to fully describe the system, a brief explanation is needed. Occasionally, these transitions will overlap such as the transition from elemental copper to chalcocite; however, are still indicated by a bold line. Lastly, aqueous species are italicized.
Figure 7-1. Component $E_\text{H}-pH$ Diagrams for Tennantite, Sulfur Oxidation limited to Elemental Sulfur. $[\text{Cu}] = 0.092 \text{ M, [As]} = 0.031 \text{ M, [S]} = 0.10 \text{ M}$. A) Copper Species, B) Arsenic Species, C) Sulfur Species.
Figure 7-2. Final Mass-Balanced $E_{\text{H}}$-pH Overlay for Tennantite, Sulfur Oxidation limited to Elemental Sulfur.

Resulting diagrams may show stability regions of two or more solid species and are accordingly labeled. Gibbs’ Phase Rule, which Gow et al. (2014d) applied to aqueous systems for the first time, dictates that the number of possible components for a quaternary system is four: water and as many as three solids. In this regard, it is noted in Figure 2 that there are several instances where, at a triple point, three solid phases are simultaneously stable: 

$$\text{Cu}_2\text{AsO}_4\text{OH} + S^0 + \text{Cu(OH)}_2, \text{Cu}_3\text{AsS}_4 + \text{Cu}_6\text{As}_4\text{S}_9 + \text{Cu}_{12}\text{As}_4\text{S}_{13}, \text{and Cu}_2\text{S} + \text{As}^0 + \text{Cu}_6\text{As}_4\text{S}_9.$$  

Two diagrams were generated for each of the copper-arsenic sulfosalt elemental compositions (see Table 2). These sets include one diagram compiled using the full thermodynamic database and one using a modified database where sulfate and other sulfoxyl species were not considered.
7.5 Results and Discussion

7.5.1 Predominant Species

Two sets of diagrams were generated for each of the copper-arsenic sulfosalt elemental compositions (see Table 2). Each set of calculated diagrams includes one diagram compiled using the full thermodynamic database (Figures 3-6), including all sulfate and oxide species. The other set of diagrams, was compiled using the modified database (Figures 7-10), which restricts sulfur oxidation to elemental sulfur, such that all sulfoxyl species were not considered, nor were the solid copper oxide species as copper hydroxide was determined to be prevalent in the alkaline testing of an enargite mineral (Gow et al., 2014a). Although initially used in previous diagrams, domeykite (Cu$_3$As) was not used in either set of diagrams, as there was no indication of its formation under the anticipated conditions (Gow et al., 2014a-b).

Table 7.2 - Elemental Composition of Copper Arsenic Sulfosalts

<table>
<thead>
<tr>
<th></th>
<th>Cu/As</th>
<th>% As</th>
<th>% S</th>
<th>As Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enargite (Cu$_3$AsS$_4$)</td>
<td>3</td>
<td>19.0%</td>
<td>32.6%</td>
<td>+5</td>
</tr>
<tr>
<td>Tennantite (Cu$_{12}$As$<em>4$S$</em>{13}$)</td>
<td>3</td>
<td>20.3%</td>
<td>28.2%</td>
<td>+3/+5</td>
</tr>
<tr>
<td>Sinnerite (Cu$_6$AsS$_9$)</td>
<td>1.5</td>
<td>30.9%</td>
<td>29.8%</td>
<td>+3</td>
</tr>
<tr>
<td>Lautite (CuAsS)</td>
<td>1</td>
<td>43.9%</td>
<td>18.8%</td>
<td>+1</td>
</tr>
</tbody>
</table>

As would be anticipated, regions of stability, particularly those of copper-arsenic mineral series vary as the individual component concentrations change. Enargite is the most stable of the four at more oxidizing conditions, followed by tennantite, and then sinnerite at increasingly reducing conditions. The indicated stability regions for each of these minerals increase when their particular mineral compositions are used to generate the mass-balanced diagrams. A free energy of formation for lautite was not included in the calculations, as the estimations of Craig...
and Barton (1973) did not include one, so no regions of stability are indicated; although, it is anticipated that the same trend would occur.

Although the stability regions of the individual copper-arsenic minerals change, the overall region where they are all stable remains relatively constant. As solution conditions become increasingly reducing, the copper-arsenic mineralization destabilizes in favor of arsenic metal and chalcocite. The arsenic oxidation state reduces from As$^{5+}$ in enargite to As$^+$ in lautite, and finally to As$^0$, Equations 1-4.

\[
\begin{align*}
4 \text{Cu}_3\text{AsS}_4 + 6 \text{H}^+ + 6 \text{e}^- & \rightarrow \text{Cu}_{12}\text{As}_4\text{S}_{13} + 3 \text{H}_2\text{S} \\
\text{Cu}_{12}\text{As}_4\text{S}_{13} + 2 \text{H}^+ + 2 \text{e}^- & \rightarrow \text{Cu}_6\text{As}_4\text{S}_9 + 3 \text{Cu}_2\text{S} + \text{H}_2\text{S} \\
\text{Cu}_6\text{As}_4\text{S}_9 + 6 \text{H}^+ + 6 \text{e}^- & \rightarrow \text{CuAsS} + 5 \text{Cu}_2\text{S} + 3 \text{H}_2\text{S} \\
2 \text{CuAsS} + 2 \text{H}^+ + 2 \text{e}^- & \rightarrow 2 \text{As}^0 + \text{Cu}_2\text{S} + \text{H}_2\text{S}
\end{align*}
\]

[Eq. 1] [Eq. 2] [Eq. 3] [Eq. 4]

The transition between each of the copper-arsenic minerals, as above, will only occur given the appropriate conditions. Discussions based on previous research of enargite reduction (Zabev et al., 2013) suggested that tennantite formations were never identified. However, tennantite formations on enargite were identified for brief periods of time via Raman Spectroscopy.
Figure 7-3. Mass-Balanced, Overlay $E_{H}$-pH Diagram for Enargite, Oxidation to Sulfate.

Figure 7-4. Mass-Balanced, Overlay $E_{H}$-pH Diagram for Tennantite, Oxidation to Sulfate.
Figure 7-5. Mass-Balanced, Overlay E<sub>H</sub>-pH Diagram for Sinnerite, Oxidation to Sulfate.

Figure 7-6. Mass-Balanced, Overlay E<sub>H</sub>-pH Diagram for Lautite, Oxidation to Sulfate.
Figure 7-7. Mass-Balanced, Overlay E<sub>H</sub>-pH Diagram for Enargite, Oxidation to Sulfur.

Figure 7-8. Mass-Balanced, Overlay E<sub>H</sub>-pH Diagram for Tennantite, Oxidation to Sulfur.
Figure 7-9. Mass-Balanced, Overlay E<sub>H</sub>-pH Diagram for Sinnerite, Oxidation to Sulfur.

Figure 7-10. Mass-Balanced, Overlay E<sub>H</sub>-pH Diagram for Lautite, Oxidation to Sulfur.
Identification of tennantite was determined by an increase in intensity of the Raman peak at 384 cm$^{-1}$, see Figure 11. The Raman peak at 384 cm$^{-1}$ is similar to the characteristic peak shown in the RRUFF database and that seen by Asbjornson et al. (2004) during a cyclic voltammetry study of tennantite surface reactivity. The brief appearance of this Raman peak correlates with the small window where tennantite would be predominant.

![Tennantite Growth vs Enargite Reference](image)

**Figure 7-11. Tennantite Growth on Enargite Surface (pH 4, -40 mV)**

It was more often noticed that the enargite surface was reduced to chalcocite, as seen in Figures 3 and 7. Within a window of only approximately 50 mV, up to four transitions are anticipated, Eq 1-4, assuming that a region for lautite would also be apparent. As seen in Figures 5 and 9, the region of tennantite is quite small. The enargite surface may have reduced directly to any of them instead of in series, as in Equation 5. The ability to identify each of these species as reaction products may prove to be difficult. Characteristics Raman peaks for sinnerite, as well as lautite, are not included in the RRUFF database, nor were any peaks identified during testing that might have identified their presence.

$$\text{Cu}_3\text{AsS}_4 + 8 \text{H}^+ + 8 \text{e}^- \rightarrow \text{Cu}_6\text{As}_4\text{S}_9 + 3 \text{Cu}_2\text{S} + 4 \text{H}_2\text{S} \quad [\text{Eq. 5}]$$
These equations represent the boundaries between the various sulfides in the region where all of the sulfides are stable. Clearly, the boundaries change with the stoichiometry of the Cu-As sulfosalt being considered. Because solids have unit activity, it is the equilibrium of H₂S with protons (H⁺) and electrons (e⁻) that defines the boundaries which, of course, corresponds directly to pH and E₄, respectively. This affect is only observed by mass-balancing the calculations of the E₄-pH diagrams and was first illustrated by Woods et al. (1987) for the ternary Cu-S-H₂O system in diagrams calculated for chalcocite (Cu₂S), djurleite (Cu₁.₉₆S), anilite (Cu₁.₇₅S) and covellite (CuS). It is the major reason why the predominant ion method should not be used to calculate anything but binary metal-H₂O systems as Pourbaix (1966) originated.

7.5.2 Elemental Sulfur vs Sulfate Oxidation

The transition from sulfide sulfur to sulfate sulfur has been determined to be particularly slow (Peters, 1984, 1986) such that oxidation beyond elemental sulfur is considered negligible. This is a practice previously employed by Woods et al. (1987) in developing aqueous Cu-S diagrams and in previous studies in this series for aqueous Cu-As-S based on enargite (Gow et al., 2014a-c). Polysulfides were included as they have stability regions under alkaline conditions.

Electrochemical profiling of a bulk enargite mineral has indicated extensive elemental sulfur formation. The sulfur content is primarily contained within copper and copper-arsenic sulfides or as elemental sulfur, as can be seen by the Cu-As-S-H₂O overlay diagrams from Gow et al. (2014a,b). Sulfur formation is prevalent across the entire pH range.

7.5.3 Arsenic and Sulfur Content

The diagrams in Figures 3-10 are organized in order of increasing arsenic content (and conversely, decreasing arsenic oxidation state). Changes within the diagrams calculated using the full data thermodynamic database, are minimal. At increased oxidation potentials, the availability
of dissolved oxygen, or similar oxygen-supplying compounds, in solution to act as a competing ligand removes the interaction between copper, arsenic and sulfur. The presence of a copper arsenate hydroxide compound is indicated in each of the diagrams. Olivenite (Cu₂AsO₄OH) appears in all calculated diagrams, which had not been determined in previous diagrams. Olivenite is one of several possible arsenate hydroxide formations, such as cornwallite (Cu₅(AsO₄)₂(OH)₂), cornubite (Cu₅(AsO₄)₂(OH)₄), or clinoclase (Cu₃AsO₄(OH)₃). Raman spectroscopy indicated the presence of such a formation, but no conclusion could be made as to which formation (Gow et al., 2014a).

The diagram for enargite and tennantite, Figures 3 and 4, also show stability regions for various copper sulfate hydroxides, brochantite (Cu₄SO₄(OH)₆) and antlerite (Cu₅SO₄(OH)). The lack of stability of these compounds in the sinnerite and lautite diagrams would indicate that some concentration or ratio threshold had been reached. The percentage of sulfur in sinnerite and tennantite is similar and there is no correlation between the copper to sulfur ratio and the stability of copper sulfate hydroxides. The only similarity that could account for their appearance would be the increased copper content, 48% in enargite up to 51% in tennantite.

When considering the diagrams where the oxidation state of sulfur is limited to 0, changes to arsenic specie stabilization, outside of the copper arsenic sulfosalt regions mentioned previously, are most prominent in the alkaline regions. The stability region of thioarsenate (AsS₄³⁻), which is the targeted species in the alkaline sulfide leaching of arsenic-bearing ores (Gow et al., 2014c), is largest when the arsenic to sulfur ratio is at its lowest of the four copper-arsenic minerals, 1:4. This region shrinks dramatically when the arsenic to sulfur ratio decreases to 1:3.25, and completely disappears at a ratio of 1:1, instead being replaced by oxy-arsenates.
As the sulfur content in the mineral increases, so does the stability of elemental sulfur. Elemental sulfur is not stable until the copper-arsenic sulfosalt mineral starts to destabilize, with the exception of enargite. There is an overlap of the two stability regions from pH 0 up to almost pH 9, which would have implications on alkaline leaching. As the pH is increased, elemental sulfur is stable down to approximately -300 mV, which was observed by prominent Raman Spectroscopy sulfur bands (Gow et al., 2014a).

7.6 Conclusions

STABCAL has been used successfully to determine mass-balanced $E_\text{H} \cdot \text{pH}$ diagrams for the Cu-As-S-H$_2$O system. In the previous study, diagrams were generated and used for the first time to show the applicability of Gibbs’ Phase Rule to an aqueous system, specifically enargite (Cu$_3$AsS$_4$). In this study, diagrams were calculated for tennantite (Cu$_{12}$As$_4$S$_{13}$), sinnerite (Cu$_6$As$_4$S$_9$) and lautite (CuAsS) for comparing to those of enargite. Stability regions within the resulting $E_\text{H} \cdot \text{pH}$ diagrams were found to vary with each mineral and attributed to differences in their stoichiometry. A particular mineral would predominate if its stoichiometry was used in the calculation. Likewise, aqueous species were also found to change and exemplified by the stability region of thioarsenate (AsS$_4^{3-}$) decreasing as the S:As ratio in the minerals decreased from 4:1 in enargite to 1:1 in lautite. Such stoichiometric effects help explain why studies on enargite leaching and electrochemistry have difficulty observing the formation of tennantite. These conclusions are the direct result of the $E_\text{H} \cdot \text{pH}$ diagrams being mass-balanced.
7.7 References


8. Future Work

Processing of enargite and other refractory copper sulfides continues to be a popular research topic at the academic and industrial levels. Many Universities have had students engaged in enargite-based research within the last few years. The following list includes many, but not all recent graduate theses:

- Alkaline sodium sulphide leaching of enargite – University of British Columbia (Torres, 2008)
- Atmospheric leaching of enargite - Queen’s University (Gupta, 2010)
- Hydrometallurgical upgrading of a tetrahedrite-rich copper concentrate – Lulea University of Technology (Awe, 2010)
- Electrochemical and leaching studies of enargite and chalcopyrite – University of British Columbia (Vasquez, 2010)
- Sulfuric acid baking and leaching of enargite concentrates- University of Utah (Safarzadeh, 2012)
- Voltammetric evaluation of enargite flotation using PAX – Montana Tech (Broden, 2014)
- Enargite treatments and pressure oxidation of concentrates – Colorado School of Mines (Conner, 2014)

Comparing the topics, it becomes obvious that the research is industry driven, with the main focus on finding process technologies. While many processes are likely feasible to go to pilot scale testing, there still remains a large gap in the fundamental aspects of enargite and both upstream and downstream aspects of the full flowsheet.

Downstream processes will require more attention as arsenic remediation remains highly problematic for any technology that attempts to co-dissolve copper and arsenic. Ferrihydrite adsorption remains an option but more novel, economical techniques need to be studied similar
to the nano-graphene platelets were in this study. Future work with functionalized nano-graphene platelets will continue at Montana Tech.

The upstream treatment of enargite has been more thoroughly examined. Any hydrometallurgical process for enargite will need to be better suited to treat an arsenic-rich concentrate instead of a whole ore leach, so the concentration method must be addressed. Selective flotation of enargite has been well addressed in recent studies at the bench-scale level by Castro and Baltierra (2003)\(^1\), and Guo and Yen (2005)\(^2\), as has selective concentration through oxidation or reduction of the enargite surface by Fornasiero et al. (2001)\(^3\). It is understood that the selective flotation is controlled by the solution potential, and must be kept within a given window dependent on the collector used. The research presented in this study would do well in conjunction with either concentration technique to enhance the fundamental understanding behind the solution potential control, similar to the study in progress at Montana Tech: Voltammetric evaluation of enargite flotation using PAX.

It is still the belief of the author that selective alkaline sulfide leach provides benefits over the acidic co-dissolution. The reductive process avoids the surface passivation issues of the high potentials needed in acidic leaching as well as simplified arsenic remediation issues, which


is in agreement with the work conducted by Anderson and Twidwell (2008a&b)\textsuperscript{4,5}. Future work should expand upon the thermodynamic study conducted here to include a more complete understanding of the alkaline sulfide system with respect to arsenic-bearing copper sulfides.


Figure A-1. SEM/MLA Analysis of an Enargite Samples from the Leonhard Mine - Butte, MT, USA
Figure A-2. SEM/MLA Analysis of an Enargite Samples from the La Libertad Mine, Quirivilca, Peru.
Figure A-3. XRD Analysis of an Enargite Samples from the Leonhard Mine - Butte, MT, USA

Figure A-4. XRD Analysis of an Enargite Samples from the La Libertad Mine, Quirivilca, Peru.
B. APPENDIX – Raw Cyclic Voltammograms

Figure B-1. Raw Cyclic Voltammogram, pH 1, scanning negative, 5 mV/s.
Figure B-2. Raw Cyclic Voltammogram, pH 1, scanning positive, 5 mV/s.
Figure B-3. Raw Cyclic Voltammogram, pH 2, scanning negative, 5 mV/s.
Figure B-4. Raw Cyclic Voltammogram, pH 2, scanning positive, 5 mV/s.
Figure B-5. Raw Cyclic Voltammogram, pH 3, scanning negative, 5 mV/s.
Figure B-6. Raw Cyclic Voltammogram, pH 3, scanning positive, 5 mV/s.
Figure B-7. Raw Cyclic Voltammogram, pH 4, scanning negative, 5 mV/s.
Figure B-8. Raw Cyclic Voltammogram, pH 4, scanning positive, 5 mV/s.
Figure B-9. Raw Cyclic Voltammogram, pH 5, scanning negative, 5 mV/s.
Figure B-10. Raw Cyclic Voltammogram, pH 5, scanning positive, 5 mV/s.
Figure B-11. Raw Cyclic Voltammogram, pH 6, scanning negative, 5 mV/s.
Figure B-12. Raw Cyclic Voltammogram, pH 6, scanning positive, 5 mV/s.
Figure B-13. Raw Cyclic Voltammogram, pH 7, scanning negative, 5 mV/s.
Figure B-14. Raw Cyclic Voltammogram, pH 7, scanning positive, 5 mV/s.
Figure B-15. Raw Cyclic Voltammogram, pH 8, scanning negative, 5 mV/s.
Figure B-16. Raw Cyclic Voltammogram, pH 8, scanning positive, 5 mV/s.
Figure B-17. Raw Cyclic Voltammogram, pH 9, scanning negative, 5 mV/s.
Figure B-18. Raw Cyclic Voltammogram, pH 9, scanning positive, 5 mV/s.
Figure B-19. Raw Cyclic Voltammogram, pH 10, scanning negative, 5 mV/s.
Figure B-20. Raw Cyclic Voltammogram, pH 10, scanning positive, 5 mV/s.
Figure B-21. Raw Cyclic Voltammogram, pH 11, scanning negative, 5 mV/s.
Figure B-22. Raw Cyclic Voltammogram, pH 11, scanning positive, 5 mV/s.
Figure B-23. Raw Cyclic Voltammogram, pH 12, scanning negative, 5 mV/s.
Figure B-24. Raw Cyclic Voltammogram, pH 12, scanning positive, 5 mV/s.
Figure B-25. Raw Cyclic Voltammogram, pH 13, scanning negative, 5 mV/s.
Figure B-26. Raw Cyclic Voltammogram, pH 13, scanning positive, 5 mV/s.
C. APPENDIX – Thermodynamic Databases

FULL DATABASE

All collected thermodynamic data. Includes nonstochiometric and metastable copper sulfides, and soluble arsenic and copper bisulfide species and single species collected throughout literature. Sources other than MINTEQ2A and USGS are listed. This diagram was used to generate the initial diagram compared against cyclic voltammetry and Raman spectroscopy results.

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔG° (kcal)</th>
<th>Ref.</th>
<th>Species</th>
<th>ΔG° (kcal)</th>
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</tr>
</thead>
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</tr>
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<td>Robie</td>
<td>Cu₁.₉₅S  Djurleite</td>
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158 | P a g e
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**Updated Database**

Copper arsenide and copper oxide species removed from consideration. Used to generate all updated \( E_{H^-} \text{-pH} \) diagrams.

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**Sulfur (solid)**

- $S$ Sulfur: 0

**Sulfur (gas)**

- $H_{2}S$: -8.041
- $SO_{2}$: -71.811

**Arsenic (aqueous)**

- $AsO_{3}^{3-}$: 102.9
- $HAsO_{3}^{2-}$: -121.105
- $H_{2}AsO_{3}$: -140.341
- $H_{2}AsO_{3}$: -152.851
- $AsO^{3-}$: -39.15
- $HAsSO_{2}^{2-}$: -79.128
- $H_{2}AsSO_{2}$: -103.412
- $H_{2}AsSO_{2}$: -98.364
- $H_{2}AsSO_{2}$: -103.412
- $AsS_{2}O_{5}^{3-}$: -77.029
- $HAsS_{2}O_{2}$: -91.763
- $H_{2}AsS_{2}O_{2}$: -101.449
- $H_{3}AsS_{2}O_{2}$: -98.175
- $AsS_{3}O^{3-}$: -38.466
- $HAsS_{3}O^{2-}$: -53.2
- $HAsS_{3}$: 0.591
- $H_{2}AsS_{3}$: -11.142
- $H_{3}AsS_{3}$: -16.19
- $AsS_{6}^{3-}$: -13.15
- $HAsS_{6}^{2-}$: -25.33

**Arsenic (solid)**

- $As_{2}O_{3}$ Arsenolite: -137.667
- $As_{2}O_{3}$ Claudetite: -137.572
- $As_{2}O_{5}$: -187.249

**Copper Arsenic (solid)**

- $Cu_{3}AsS_{4}$ Enargite: -49.808
- $Cu_{3}AsS_{6}$ Sinnerite: -110.256
- $Cu_{12}As_{4}S_{13}$ Tennantite: -180.908
- $Cu_{3}(AsO_{3})_{2}2H_{2}O$: -424.227
- $Cu_{2}AsO_{4}OH$: -201.9

**References**

- Ref. to Robie
- Ref. to Craig
- Ref. to Barin
- Ref. to Nishimura
**Oxidation Limited to Elemental Sulfur**

In addition to species removed in the Updated database, all copper and arsenic sulfoxy species are removed. Used to generate all E$_H$-pH diagrams where oxidation is limited to elemental sulfur.

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<th>$\Delta G^\circ$ (kcal)</th>
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</tbody>
</table>
D. APPENDIX - Arsenic Remediation using a Novel Nano-Graphene Material

A. Cruise¹, R.N. Gow¹, C. Young², and J. Bowden³

¹FLSmidth USA Inc., 7158 S FLSmidth Dr, Midvale, UT, 84047
²Montana Tech of The University of Montana; 1300 W. Park; Butte, MT, 59701
³Simbol Materials; 1536 Jones St; Brawley, CA, 92227

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Abstract

As enargite and tennantite become viable sources of copper and become more associated with gold ores, a hydrometallurgical remediation process for arsenic will need to be a necessary step in meeting EPA regulations. The current discharge limit of arsenic in wastewater is 10 ppb. The EPA lists arsenic adsorption by ferrihydrite as the Best Developed Available Technology. However, carbon-based adsorbents such as carbon nanotubes and nanographene can be used as an easier, higher surface area option. Nanographene platelets (nGP), which provide a higher surface area than nanotubes, were tested for their adsorption characteristics of arsenic. A sample of nGPs was received by the Undergraduate Research Program at Montana Tech for a bench-scale experimental design considering the initial arsenic concentration, residence time and temperature. The maximum adsorption capability of nGPs was approximately 1500 mg As per g nGP at 20 °C and 800 mg As at 40 °C. The adsorption values were modelled using the Stern-Langmuir isotherm, which then allowed for a thermodynamic evaluation of the process. Free energy of adsorption was calculated at approximately -3.9kcal/mol at both 20 and 40°C, suggesting a spontaneous process, characterized by physisorption. At no point was the arsenic level dropped below the EPA limitations. Based on the identification of a physisorption process, no further testing of this material was conducted. Instead, testing on a functionalized version of a nGP will be conducted next.
Introduction

Arsenic is considered a toxic substance by the EPA, and as such the discharge of industrial processes is monitored. Mines based in the U.S. must lower the arsenic content of their waste streams below 10 parts per billion. This becomes difficult at copper and gold mines with arsenic-bearing minerals such as enargite and tennantite. The arsenic becomes heavily concentrated as these minerals are separated out into what can be termed as “dirty cons” and then leached under highly acidic conditions, like those in Galvanox or CESL processes.

Authors Twidwell and McCloskey, of Montana Tech, compiled previously published research on the topic of arsenic remediation and long term storage (2011). Previous authors have attempted to treat arsenic-bearing wastewater by co-precipitation of arsenic with calcium, through formation of calcium arsenates; although, it was determined that this method was not appropriate for long term storage of arsenic waste (Robins and Tozawa, 1982). Other research has included precipitation of arsenic within a phosphate matrix, cementation using zero valence iron (Twidwell and Hadden, 2004; Twidwell and Sundberg, 2005), and adsorption on the surface of the iron oxyhydroxides, such as ferrihydrite and aluminum modified ferrihydrite (Twidwell, 2007; Twidwell, 2008; Twidwell and Leonhard, 2008). The EPA has identified ferrihydrite adsorption as the current Best Demonstrated Available Technology (BDAT).

Carbon nanotubes (CNTS) have also received a large amount of attention for their ability to adsorb metal and organic compounds. Several authors have examined the ability of CNTs to remove contaminants such as chromium, lead, and copper (Sheng et al., 2010; Gupta et. al., 2011a, b; Ren et al., 2012) among others.

Nano-graphene platelets (NGPs) are a more recent creation in the realm of high surface area carbon-based adsorbents (Jang and Zhamu, 2008). They have an estimated surface area of
more than 2600 m²/g, more than twice that of CNTs, which is anticipated to provide higher adsorption capabilities.

Montana Tech received a sample of NGPs from Russian based Petrov-gNP. The Undergraduate Research Program, in conjunction with the Metallurgical and Materials Engineering Department began a preliminary study to test their ability for arsenic adsorption and provide a thermodynamic evaluation of the process.

**Materials and Methods**

The adsorption capabilities of the received NGPs were tested on solutions of arsenate (As⁵⁺) and arsenite (As³⁺) over the pH range 2-10 to determine the solution conditions at which the highest arsenic removal was obtained. Arsenic and nPG concentrations were held constant in each test at 0.10 M and 0.10 g respectively.

Once the optimal pH was identified, a full factorial design of experiment (DOE) was created using StatEase, a statistical analysis program. As would be expected of an adsorption process, initial arsenic concentration, residence time and starting temperature were indicated as variables. The full design, including three midpoint tests to determine repeatability, can be seen in Table 1. Arsenate concentration was varied from 1.0x10⁻³ M to 1.0x10⁻¹ M, for either 1 or 5 hours, at temperatures of 20 °C or 40 °C.

Buffer solutions were created for pH 2, 4, 6, 8 and 10 according to the CRC Handbook (Haynes, 2011), using 18.2 MΩ water. Appropriate amounts of sodium arsenate dibasic heptahydrate (Na₂HAsO₄●7H₂O, Sigma-Aldrich, >98%) and sodium (meta)arsenite (NaAsO₂) Sigma-Aldrich, >90%) were dissolved in each buffer solution. Each test used 100 mL of solution in a 250 mL Erlenmeyer flasks with 0.10g of NGPs. Flasks were covered with Parafilm and then agitated using a flask shaker table.
Table 1 - Arsenic Adsorption Design of Experiment

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<th>Time (hrs)</th>
<th>Temperature (C)</th>
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<td>0.001</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>0.001</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>0.001</td>
<td>5</td>
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<tr>
<td>4</td>
<td>0.001</td>
<td>5</td>
<td>40</td>
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<tr>
<td>5</td>
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<td>0.100</td>
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<td>8</td>
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<tr>
<td>9</td>
<td>0.050</td>
<td>3</td>
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<tr>
<td>10</td>
<td>0.050</td>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>0.050</td>
<td>3</td>
<td>30</td>
</tr>
</tbody>
</table>

Inductively coupled plasma (ICP) was used to determine solution concentrations for each test before and after the allotted time, to track concentration changes. Adsorption capacity values, $\Gamma$, were then calculated based on the difference in arsenic concentration.

**Experimental Results – pH**

Similar to adsorption of arsenic by ferrihydrite, the optimal pH is close to 6, as seen in Table 2. Approximately 35% of arsenite and arsenate was adsorbed at pH 6. A slightly higher percentage of arsenate was removed at pH 10, 36.3% vs 34.6%; although the adsorption capacity of the nGPs is very similar at approximately 150 mg As per gram of nGP. The highest adsorption capacity was seen with arsenate, at 229 mg As per gram nGP. Based on these results, the DOE was conducted using arsenate-containing buffer solutions, at pH 6.

**Experimental Results – DOE**

Results from the experimental design are listed in Table 3. At no point was the arsenic solution concentration dropped into the part per billion range. The lowest concentration achieved was approximately 33 ppm; although adsorption capacities as high as 664 mg per gram nGP.
Table 2 - Arsenic Adsorption by pH

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<th>pH</th>
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<th>Final Concentration (ppm)</th>
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<th>% As removal</th>
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</thead>
<tbody>
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<td>488</td>
<td>39</td>
<td>7.4</td>
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</table>

Arsenate

<table>
<thead>
<tr>
<th>pH</th>
<th>Initial Concentration (ppm)</th>
<th>Final Concentration (ppm)</th>
<th>( \Gamma ) (mg As / g nGP)</th>
<th>% As removal</th>
</tr>
</thead>
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<td>411</td>
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</table>

Arsenite

were achieved. It may be possible that the addition of larger amounts of nGP, or by testing the adsorption process in a counter current fashion, would further reduce the arsenic solutions concentrations.

It can be seen that there is a large range of initial concentration solution, which are lower than the expected 0.1 M, or 1000 ppm. There may have been buffer interactions that are not currently accounted for as each pH buffer makeup was slightly different. It is not known how arsenite and arsenate reacted with each buffer. Further testing should instead have the pH controlled using NaOH and HCl.

It should also be noted that there were handling and solution contact issues throughout the testing. The nGP material contained a static charge which interacted with the weigh scale and the plastic weighing containers, causing unexpected material losses at times. A 0.10 g portion of nGP was used in each test to minimize any small volume losses due to this effect. Secondly the nGPs could not break the surface tension of the arsenic-solution, instead maintaining contact
Table 3 - Arsenate Adsorption Experimental Design

<table>
<thead>
<tr>
<th>Test #</th>
<th>Initial As Concentration (M)</th>
<th>Time (hrs)</th>
<th>Temp (C)</th>
<th>Initial Concentration (ppm)</th>
<th>Final Concentration (ppm)</th>
<th>Γ (mg As / g nGP)</th>
<th>% As removal</th>
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</thead>
<tbody>
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</tbody>
</table>

only at the surface-air interface. The shaker table used to agitate the solutions did not provide enough turbulence to provide adequate contact. It is likely that the adsorption capacity values were underestimated, and would be better determined using a more appropriate mixing method.

The poor mixing is likely what led to the lack of reproducibility within the midpoint tests, tests 9-11. The three tests had an average of 13.6 mg As removed per g nGP, with a relative standard deviation of greater than 100%. At this large of an estimated error, it becomes difficult to identify significant differences between results. For the sake of obtaining thermodynamic information the results the mid-point results will not be considered.

**Thermodynamic Evaluation**

Similar to a carbon-based adsorption study conducted by Young et al. (2011), the adsorption process can be modelled using an adsorption isotherm. In this case the Stern-Langmuir isotherm is used, which applies to reversible and equilibrium adsorption process, Eq 1:

\[ K = \frac{\theta}{(1-\theta)C} = \frac{k_1}{k_2} \]  

[Eq. 1]
where $\theta$ is the fraction of surface coverage, $K$ is the equilibrium constant between the adsorption ($k_1$) and desorption ($k_2$) rate constants, and $C$ is the equilibrium concentration of the adsorbing species (M). The equilibrium constant, $K$, can then be introduced into one form of Gibbs’ free energy equation to determine $\Delta G_{ads}$ (kcal/mol), Eq. 2:

$$\Delta G_{ads} = -2.303RT \log(55.55K) \quad [\text{Eq. 2}]$$

where 55.55 is the molar concentration of water.

Since the adsorption process is conducted at two different temperatures, the Clausius-Clapeyron equation is used to estimate the enthalpy of adsorption, Eq. 3.

$$\Delta H_{ads} = \frac{\Delta (\frac{\Delta G_{ads}}{T})}{\Delta (\frac{1}{T})} \quad [\text{Eq. 3}]$$

Lastly, the entropy of adsorption is determined via rearrangement of Gibbs’ fundamental equation, Eq. 4.

$$\Delta S_{ads} = \frac{(\Delta H_{ads} - \Delta G_{ads})}{T_{avg}} \quad [\text{Eq. 4}]$$

The fraction of surface coverage is determined by comparing the adsorption capacity values, $\Gamma$, against a maximum adsorption values, $\Gamma_{max}$, Eq. 5, determined by regression analysis, seen in Figure 1.

$$\theta = \frac{\Gamma}{\Gamma_{m}} \quad [\text{Eq. 5}]$$

The maximum adsorption values, $\Gamma_{max}$, for this study are estimated at 1500 mg As per g nGP at 20 °C and 800 mg As at 40 °C. The R-squared values for the regression analysis are not optimal, particularly at 40°C, $R^2 = 0.6015$. The previously described material handling issues could partially be responsible.
The equilibrium constant, $K$, was determined at each temperature by a linear regression of the surface coverage portion of Eq. 1, $\theta/(1-\theta)$, plotted against the equilibrium concentrations, Figure 2. The $K$ values are used to complete the thermodynamic analysis, which can be seen in Table 4.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$\Delta G_{ads}$ (kcal/mol)</th>
<th>$\Delta H_{ads}$ (kcal/mol)</th>
<th>$\Delta S_{ads}$ (cal/mol/$^\circ$K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-3.86</td>
<td>-2.81</td>
<td>3.48</td>
</tr>
<tr>
<td>40</td>
<td>-3.94</td>
<td>-2.81</td>
<td>3.48</td>
</tr>
</tbody>
</table>

Table 4 - Thermodynamic Data for Arsenic Adsorption on Nano-graphene Platelets

Figure 1. Regression Analysis for Maximum Adsorption Capacity, $\Gamma_{max}$
The large difference in maximum adsorption values at 20 and 40 °C would suggest that there is a large temperature-driven aspect to the process; however, based on the negative enthalphy and positive entropy values the reaction should be spontaneous at any temperature.

The overall adsorption process is determined to be spontaneous, based on the negative free energy of adsorption values; although, it is only slightly so based on the magnitude of the values. Additionally, since the free energy is more positive than -5 kcal/mol, the adsorption process would be expected to be physisorption as opposed to chemisorption. The weaker bonding inherent in physisorbed processes is much weaker and is not likely to withstand a long-term storage.
Further Testing

Based on the physisorption determination, a second sample of nGP material was provided to Montana Tech. This nGP sample was functionalized to improve adsorption capabilities and more strongly adsorb the arsenic.

There are a number of material handling issues that can be better handled when testing the functionalized nGP material. As mentioned previously, pH will be controlled by NaOH and HCl to remove any buffer interactions. The material handling issues can be mitigated by containing any nGP material within a mesh container within the solutions, similar to technologies used for carbon-in-pulp processing. This should maximize the solution contact and improve results.

Conclusions

An initial series of tests identified the maximum adsorption of both arsenite and arsenate species on nano-graphene platelets (nGP) at pH 6. This is consistent with studies done on the adsorption of arsenic on the surface of ferrihydrite. Further testing indicates that the maximum adsorption capacity of the nGPs was approximately 1500 mg As per g nGP at 20 °C and 800 mg As at 40 °C. A thermodynamic analysis of the adsorption process determined the free energy of adsorption to be approximately -3.9 kcal/mol at either temperature, suggesting the process is spontaneous but is characterized as physisorption.

There were material handling issues with the nGP material that could improve upon the results in this study. A combination of the material’s light weight and hydrophobicity led to inefficient mixing and solution contact. It is possible that a larger amount of nGP material, added in stages, in a well-mixed system could possibly reduce the arsenic concentration in solution below the EPA limit of 10 ppb; however, since the arsenic is weakly held by a physical bond, it
is unlikely that nano-graphene platelets would be useful for long term storage for arsenic remediation. It is anticipated that a functionalized nGP material will improve upon the results seen in this study.

Acknowledgements

The authors would like to thank the Undergraduate Research Program at Montana Tech for their support and guidance, and Petrov-nGP for providing the graphene material used for testing. The Undergraduate program and this research are partially responsible for the paths pursued by Allyse Cruise, who now works for FLSmidth in their mineral research and testing facility, and Jesse Bowden, who has since completed her Master’s Degree in Metallurgical Engineering and now works for Simbol Materials.
References


