Spectroelectrochemistry of Enargite III: Alkaline Sulfide Leaching

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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 E_H-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 solubilise, 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, as well as guidance for control of reagents and solution potential and, of course, the need for water treatment afterwards.

Introduction

Environmental limitations on pyrometallurgical processing of arsenic-bearing concentrates have forced operations to consider other solutions. Attempts to hydrometallurgically process enargite (Cu₃AsS₄) 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 (Cu₂S) 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 (Achimovicova et al., 1999; Anderson and Twidwell, 2008a,b; Tongamp et al., 2009 and 2010), hypochlorite (Vinals et al., 2003; Curreli et al., 2005; Mihaljovic et al., 2007), ammoniacal (Gajam and Raghavan, 1983), and acid (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_2S_3), enargite and tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$) are solubilized as thioarsenite (AsS_3^{3-}) and thioarsenate (AsS_4^{3-}) according to Equations 1-3 (Filippou et al., 2007):

As indicated, orpiment completely solubilizes and, depending on the type of copper mineral being leached, either chalcocite (Cu_2S) or an anilite-like ($\text{Cu}_{1.714}\text{S}$) phase forms. However, it is understood that covellite (CuS) and other nonstoichiometric copper sulfides (Cu_xS) may form as well, depending on the redox chemistry of the system (Woods et al., 1987). The antimony sulfosalt series, stibnite (Sb_2S_3) and tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) are known to behave relatively similarly (Awe and Sandstrom, 2010).

Several recent studies have improved upon the kinetics of arsenic leaching 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: 85.8 kJ/mol according to the National Bureau of Standards (NBS) (Wagman et al., 1982) database or 111.4 kJ/mol according to the MINTQA2 (Allison et al., 1990) database used in this study. Using the Minteq 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 sulfoxy species (e.g., thiosulfate, $\text{S}_2\text{O}_3^{2-}$; sulphite, 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_9S_5) and covellite were identified after six hours, while 97% of the arsenic was leached. Bornite (Cu_5FeS_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_5S_3 , perhaps the same undetermined species reported by Achimovicova (1999), Balaz (2000) and Balaz and Achimovicova (2006) by mechanical activation.

The finding 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).

Figure 1 - E_H-pH Diagram for Sulfur, 1M, using MinteqThermodynamic Data and Assuming Oxidation to Elemental Sulfur Only Ignoring all Sulfoxy Ions

Figure 2 - E_H-pH Diagram for the Cu-S-H₂O system, considering all copper thio-complexes. Cu = 10⁻⁵ M, S = 1 M (Young et al, 2003)

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.

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 and 4. 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,B). At or below this ratio, only arsenic should solubilize, leaving behind the 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, AsS₄³⁻, stability is seemingly unchanged across the stability diagrams, suggesting that the Cu/S ratio is important to selectively leaching arsenic.

Table 1: Free Energy Values for Copper and Arsenic Thio-complexes
(¹Young et al., 2000; ²Young et al., 2003)

Cu Species ²	ΔG (kcal)	As Species ¹	ΔG (kcal)
Cu(HS) ₂ ⁻	-5.68	AsS(OH)(HS) ⁻	-58.58
Cu ₂ S(HS) ₂ ²⁻	-8.11	AsS(HS) ₂ ⁻	-9.08
CuHS ⁰	-2.85	As ₃ S ₅ (HS) ²⁻	-25.33
Cu(HS) ₃ ⁻	-11.94	HAs ₃ S ₄ (HS) ₂	-43.02
CuS(HS) ₃ ³⁻	-0.85	As ₃ S ₄ (HS) ₂ ⁻	-33.22

Sample Analysis

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 ½” x ½” 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).

Figure 3: Mass-balanced E_h -pH Diagrams for the Cu-As-S system, $50 \text{ g L}^{-1} \text{ Na}_2\text{S}$. Top row shows copper-bearing species while the bottom row shows arsenic-bearing species. Shaded regions indicate where dissolution occurs.

A & B) 10^{-3} M Cu/As C & D) 10^{-5} M Cu/As E & F) 10^{-7} M Cu/As

Figure 4: Mass-balanced E_h -pH Diagrams for the Cu-As-S system, 250 g L⁻¹ Na₂S. Top row shows copper-bearing species while the bottom row shows arsenic-bearing species. Shaded regions indicate where dissolution occurs.

A & B) 10⁻³ M Cu/As C & D) 10⁻⁵ M Cu/As E & F) 10⁻⁷ M Cu/As

Raman Spectroscopy

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_2S) was added to each buffer solution yielding concentrations of either 50 or 250 g L^{-1} . Sulfide concentration levels were identified from other similar studies (Nadkarni and Kusik, 1988; Awe and Sandstrom, 2010; Tongamp et al., 2009).

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_2S solutions, a series of new peaks formed that were not identified. An example is shown in Figure 5 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 5, 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 Figure 4 for enargite at 250 g L^{-1} .

Figure 5 – Raman spectra of enargite (bottom) compared to enargite reacted at pH 12 and -300 mV with 250 g L^{-1} Na_2S (middle) and resulting evaporate crystallized out of solution (top)

At pH 12 and 250 g L⁻¹ Na₂S, Figure 4 predicts that enargite will dissolve as CuS(HS)₃³⁻, Cu₂S(HS)₂²⁻ or Cu(HS)₃⁻ and, when the potential is -300 mV, CuS(HS)₃³⁻ is expected to predominate. Upon evaporation, these species would crystallize out, perhaps as the aqueous copper sulfide identified as NaCu₅S₃ 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. Na₂S 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_xS (where 2 ≤ x ≤ 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 2: Leaching Conditions used by Previous Authors (adapted from Torres, 2011)

Author	% Cu in Material	Highest conc. Na ₂ S (g L ⁻¹)	Amount solids tested (g L ⁻¹)	Maximum S/Cu Ratio Observed	NaOH conc. (g L ⁻¹)	Copper Sulfide Product
Achimovicova et al. (1999)	39	100	4	52	50	Cu _{1.4} S
Anderson and Twidwell (2008a,b)	18	100	250	2	20	-
Curreli (2009)	33	33	10	8	100	Cu _{1.52} S, Cu ₂ S
Gow et al. (this study)	44 (avg)	250	electrode	---	pH 11-13	CuS, Cu ₂ S
Nadkarni and Kusik (1988)	25	160	363	2	1.5	Cu ₂ S
Tongamp (2009)	33.7	200	100	5	50	Cu ₂ S
Torres (2011)	32	80	50	4	100*	CuS, Cu _{1.8} S, NaCu ₅ S ₃ (aq)

Cyclic Voltammetry

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.

Cyclic voltammograms (CV's) determined in the presence of Na₂S were compared to those determined in its absence (Gow et al., 2014a). An example is shown in Figure 6 for results obtained at pH 13. Results suggest that reactions appear and/or shift to lower potentials with the increasing addition of Na₂S. It was determined that, in the absence of Na₂S, selective arsenic dissolution occurred at an average potential of -300 mV over the pH range 11-13 according to the following oxidation reaction:

Elemental sulfur (S⁰) 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 C₁ 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 C₁ is not the reverse of Reaction A₁; rather, it is a series of reduction reactions involving the products as previously explained for the absence of Na₂S.

Figure 6 – Cyclic Voltammograms of Enargite at pH 13 in the presence of 250 g L⁻¹ Na₂S (top) and 50 g L⁻¹ Na₂S (middle) compared to its absence (bottom). See text for reaction details.

When Na₂S is added to the system, it equilibrates with bisulfide (HS⁻) and reacts with elemental sulfur to form polysulfide (see Figure 1):

where y = 1 to 4. Thus, if elemental sulfur forms as with Reaction A₁, it will be consumed and surface passivation will therefore be prevented. Figure 6 clearly shows that various cathodic reactions are unmasked and, furthermore, that current flow increases with increasing Na₂S 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 A₁, thioarsenate (AsS_4^{3-}) will form instead (see Figures 3 and 4):

Reactions A₁ and A₂ explain how covellite can be observed in the absence and presence of Na_2S . Like Reaction C₁, the reverse reaction cannot occur because enargite is unstable under these conditions. Reaction C₂ therefore involves each of the products undergoing a series of reduction reactions.

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:

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

Thus, by combining Reactions 8 and 10 as well as Reactions 9 and 11, the following reactions result, respectively:

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 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_5S_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):

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:

This is Reaction C₄ and ultimately accounts for the array of peaks that appear in Figure 6 as C_{4a-d} and A_{4a-d}.

AsS₄³⁻ Reduction

According to Figures 3 and 4, AsS₄³⁻ may undergo two reduction reactions, first to HAsS₃²⁻ and then As⁰:

At high solution pH > 8, it is anticipated this occurs rapidly and the two equations may be combined such that:

Although As⁰ 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 C₅ and C_{3b}, respectively. These reactions yield Cu⁰ which occurs near the same potentials as As⁰ formation.

Mass Balanced Diagrams

Mass-balanced E_H-pH diagrams are presented in Figure 7A and B, overlaid for copper and arsenic containing species, considering 50 and 250 g L⁻¹ Na₂S 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 disagreement 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 7- Mass-balanced E_H-pH Diagrams for the Cu-As-S system; 3x10⁻⁵ M Cu and 1x10⁻⁵ M As; and S oxidation to sulfide only with A) 50 g L⁻¹ Na₂S and B) 250 g L⁻¹ Na₂S. 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

It is understood that the alkaline sulfide leaching of gold involves conditions similar to those tested here and that sulfide is the likely lixiviant with polysulfide the oxidant that leads to the formation of AuS^- (Jeffrey and Anderson, 2003). However, like As and Cu, bisulfide can also leach gold by forming $\text{Au}(\text{HS})_2^-$ (Seward et al., 1973). Aside from these three elements, a number of others are known to form bisulfide complexes: Ag, Pt, Pd, Zn, Hg and Sb (Barnes, 1997). While most of the early interest has been on developing thermodynamic data to understand how metals are transported and deposited geologically, recent applications have been about developing hydrometallurgical processes for extracting and recovering the metals.

For enargite, 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. This appears to be related to the S:Cu molar ratio and thermodynamic calculations suggest this ratio should be 640:1 explaining why the Na_2S 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_2S addition, selective alkaline leaching could be done between pH 11-13 and E_{H} -600 to -300 mV. The results of this study in the presence of Na_2S has shown that the E_{H} range of 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_y^{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_2S 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.

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