The Application and Economics of Industrial Alkaline Leaching of Copper Enargite Concentrates

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As demand for copper and precious metals continues to grow, the need to develop new supplies increases. In the imminent future, the new large global ore bodies are more complex, with enargite, tennantite and tetrahedrite as the abundant contained mineralogy. These resources also contain considerable gold and silver. As such, direct treatment by conventional smelting is prohibitive due to the potential environmental impacts and copper quality issues. This paper outlines the effective application and associated economics of industrially proven Alkaline Sulfide Leaching (ASL) hydrometallurgical technology to an enargite concentrate for selective removal and recovery of arsenic, antimony, gold and silver, leaving a clean high-grade copper concentrate. The fundamentals behind the technology are described, along with those of hydrometallurgical arsenic fixation and stabilization. Flowsheets and unit operations are elucidated, along with an in-depth economic analysis.

INTRODUCTION

Hydrometallurgical methods can be employed for treatment of gold-, arsenic-, antimony-, tin- and mercury-containing materials, concentrates and ores, as well as complex ones containing any number of metals (Conner & Anderson, 2013). The alkaline sulfide leaching (ASL) system is one of these. It is essentially a mixture of sodium sulfide and sodium hydroxide with other meta-stable alkaline species as required. This is a unique hydrometallurgical system beause it is a very selective lixiviant for the distinct leaching of tin, gold, antimony, arsenic, tellurium, silver and mercury (Anderson, 2000, 2001a, 2001b, 2002, 2003, 2012, 2014; Anderson & Twidwell, 2008a, 2008b, 2010; Anderson et al., 2004, 2005; Glazkov & Tseft, 1961; Gnatyshenko & Polyvyanni, 1961; Nadkarni et al., 1975; Nadkarni & Kusik, 1988; Polyvyanni, 1963). Worldwide, ASL technology has been employed industrially in the former CIS, China and the United States for the production of antimony (Anderson et al., 1992, 1994; Anderson & Krys, 1993; Holmes, 1944; Kaloc, 1967; Nordwick & Anderson, 1993; van Stein, 1971).

As an example, when the alkaline sulfide hydrometallurgical system is applied to an arsenic-containing material like orpiment, As_2S_3, a sulfide-complexed species of sodium thioarsenite in solution is formed. This is illustrated as:

$$Na_2S + As_2S_3 \rightarrow 2NaAsS_2 \qquad [1]$$

$$NaAsS_2 + Na_2S \rightarrow Na_3AsS_3 \qquad [2]$$

When applied to arsenic trioxide, As_2O_3, sodium arsenite is also formed but the oxides generate hydroxide. The reaction is as follows:

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$$1.5 \ H_2O + 2 \ Na_2S + \frac{1}{2} \ As_2O_3 \rightarrow \ NaAsS_2 + 3 \ NaOH \tag{3}$$

$$NaAsS_2 + Na_2S \rightarrow Na_3AsS_3 \tag{4}$$

Dissolution of elemental sulfur in sodium hydroxide is also used as a lixiviant for alkaline sulfide leaching of arsenic. The combination of sodium hydroxide and elemental sulfur results in the formation of species other than just sulfide (S^{-2}). Both sodium polysulfide (Na_2S_x) and sodium thiosulfate ($Na_2S_2O_3$) are created along with sulfide. Figure 1 illustrates the equilibrium diagram for sulfur while Figure 2 illustrates the metastable sulfur diagram more commonly encountered and utilized in ASL industry applications.
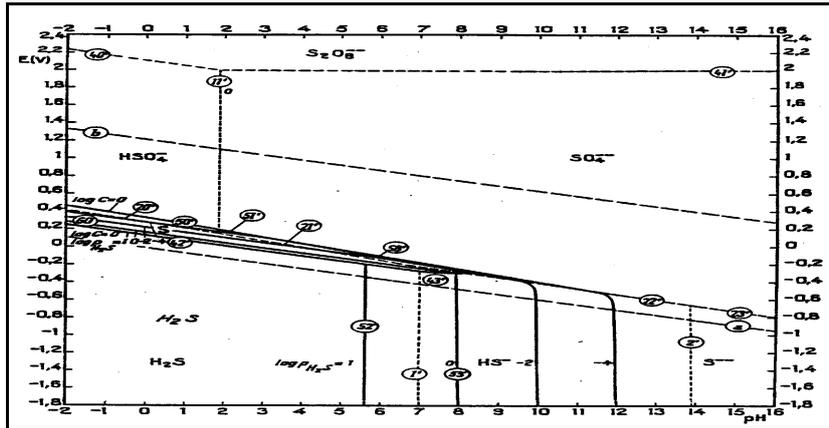

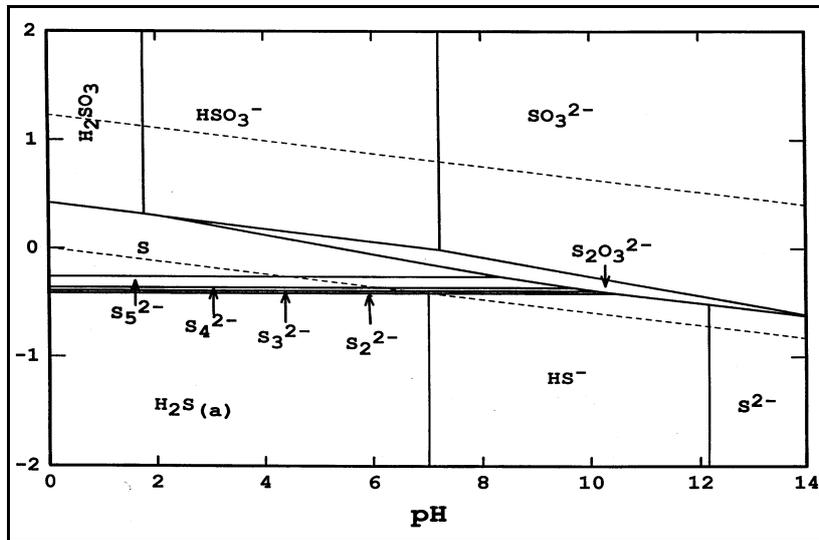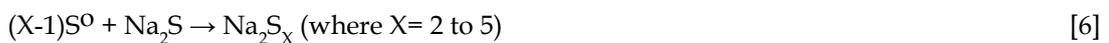Figure 1. Equilibrium potential/pH (Eh-pH) diagram for sulfur (Pourbaix, 1966).

Figure 2. Meta-stable potential/pH (Eh–pH) diagram for sulfur (Huang, 2007).

The generation of these predominant meta-stable species is illustrated simplistically in the following scenario:

$$4S^O + 6NaOH \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O \tag{5}$$

$$(X-1)S^O + Na_2S \rightarrow Na_2S_X \ (\text{where } X= 2 \text{ to } 5) \tag{6}$$

Due to the oxidizing power of polysulfide on sodium thioarsenite, the major species in solution is normally sodium thioarsenate (Na_3AsS_4). This can be viewed as follows:

$$Na_2S_X + (X-1)Na_3AsS_3 \rightarrow (X-1)Na_3AsS_4 + Na_2S \qquad\qquad [7]$$
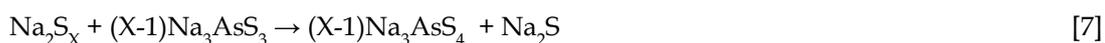
Fundamental information and data on this technology is very limited or it is restricted. Due to space constraints in this paper, the few other available illustrative Pourbaix Eh pH diagrams in the alkaline sulfide system may be found in the referenced literature (Anderson, 2003; Anderson et al., 2005; Robins, 2000; Tian-cong, 1988; Young & Robins, 2000).

As shown in Figure 3, gold is soluble and very stable in the alkaline sulfide system. Gold lixiviation is the result of leaching by polysulfide oxidation and sulfide complexation, as shown in Equation 8 (Anderson, 2001a; Anderson et al., 2004, 2005; Jeffrey & Anderson, 2002):
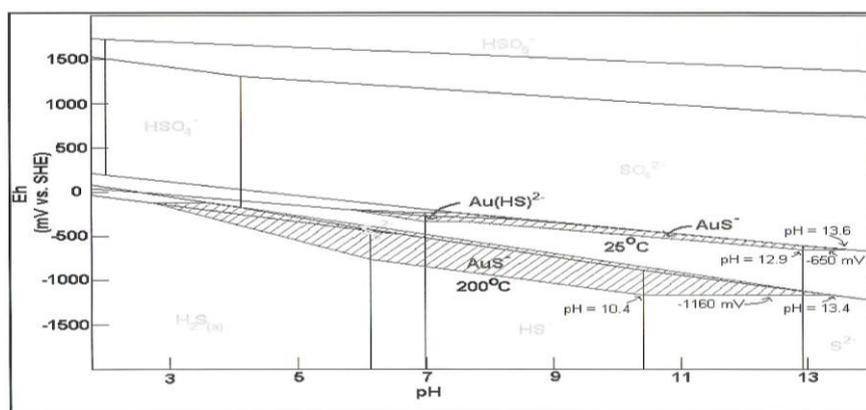
$$2Au + S_2^{2-} + 2S^{2-} \rightarrow 2AuS^- + 2S^{2-} \qquad\qquad [8]$$

Figure 3. Equilibrium species Eh–pH diagram for 100 mg/L Au in 1 M solution at 25 °C and 200 °C. (Anderson et al., 2004.)

Gold leached by the alkaline sulfide system is separable by solvent extraction, activated carbon and ion exchange and recoverable by several means including cementation, electrowinning, ionic reduction and non-ionic reduction. Conventional methods of gold recovery, such as zinc or aluminium cementation, are not applicable to this type of solution because of the dangers associated with stibine or arsine gas generation.

A proprietary gold recovery practice (Anderson, 2001a) has been adopted at the pilot-plant scale to quantitatively and selectively recover gold from complex alkaline sulfide solutions containing a mixture of metals such as arsenic, tin, mercury and antimony. This is illustrated by selectively removing gold from an alkaline sulfide leach solution containing these impurities. The assays of the solution tested and final products are shown in Table I. The overall results are presented in Table II.
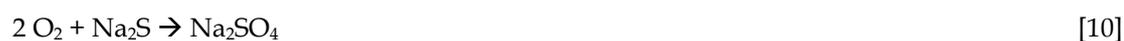
Table I. Alkaline sulfide leach initial and final solution assays.

Solution	Volume (L)	Au (mg/L)	Sb (g/L)	As (g/L)	Hg (mg/L)	Sn (g/L)
Initial	0.5	88.7	21.0	5.31	274	1.84
Final	0.5	14.4	21.1	5.21	274	1.89

Table II. Overall elemental distribution.

Element	Distribution to liquid (%)	Distribution to solid (%)
Gold	1.7	98.3
Antimony, arsenic, tin, mercury	100	0.0

The waste alkaline sulfide solutions can be recycled for further gold leaching or further processed with low temperature oxidation to sodium sulfate, Na_2SO_4. This also oxidizes the arsenic to soluble sodium arsenate which can then be precipitated by conventional means using iron compounds. This oxidation process has been practiced in industry (Edwards, 1985). The resultant sodium sulfate, after arsenic removal, is further treated by purification and crystallization to produce high-grade, marketable sodium sulfate. This process is illustrated simplistically in the following scenario:

$$Na_3AsS_4 + 2\,O_2 \rightarrow Na_3AsO_4 \tag{9}$$

$$2\,O_2 + Na_2S \rightarrow Na_2SO_4 \tag{10}$$

$$3.5\,O_2 + 2NaOH + Na_2S_2 \rightarrow 2Na_2SO_4 + H_2O \tag{11}$$

$$8\,O_2 + 8NaOH + Na_2S_5 \rightarrow 5Na_2SO_4 + 4H_2O \tag{12}$$

$$2\,NaOH + 2\,O_2 + Na_2S_2O_3 \rightarrow 2Na_2SO_4 + H_2O \tag{13}$$

This versatile and environmentally benign chemical may then be sold to and utilized in industries, such as pulp and paper, glass, ceramics, detergents, textile dyes, mineral feed supplements, bleach and photography. As such, there are minimal environmental or toxicological issues in the use of alkaline sulfide gold recoveries because the waste products become value-added, marketable by-products. The sodium sulfate produced can be used to regenerate the sodium hydroxide needed in the process in a manner analogous to industrial dual alkali scrubbing systems (Lunt et al., 2003). This is as follows:

$$2\,Na_2SO_4 + Ca(OH)_2 + 2\,H_2O \rightarrow CaSO_4{:}2H_2O + 2NaOH \tag{14}$$
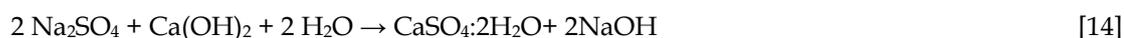
The clean gypsum product can then be marketed and used in such applications as agricultural soil amendments or as an additive in primary cement manufacture. In addition, efforts have been successfully confirmed in regenerating H_2SO_4 and NaOH reagents from the Na_2SO_4 byproducts using electrodialysis, as noted in reaction 15:

$$Na_2SO_4 + 2H_2O \leftrightarrow H_2SO_4 + 2NaOH \tag{15}$$

Traditionally, the ASL system was used to produce antimony metal and sodium antimonate from tetrahedrite concentrates at Sunshine Mining and Refining for nearly six decades (Anderson & Krys, 1993; Nordwick & Anderson, 1993). This industrial ASL flowsheet, as it stood when it last operated in 2001, is shown as Figure 4. Note the use of dissolved elemental sulfur in the flowsheet and not pure sodium sulfide.

AQUEOUS ARSENIC REMOVAL PROCESSES

In conjunction with ASL technology, arsenic must be selectively precipitated, stabilized and managed. The removal of arsenic from process solutions and effluents has been practiced by the mineral industries for many years (Anderson et al., 2014). In their recent publications, Paktunc and coworkers provided a clear description of the influence of pH and Fe/As ratio on what phases may form and their transformation to other products (Paktunc & Bruggeman, 2010; Paktunc et al., 2008). They have eliminated a long-standing controversy concerning what phases form. The understanding of arsenic removal has matured immensely. Hence, removal by existing hydrometallurgical techniques is adequate for present-day product specifications but the stability of waste materials for long-term disposal may not meet the regulatory requirements of the future. The various arsenic separation methods include: oxidation–reduction, adsorption, electrolysis, solvent extraction, ion exchange,

membrane separation, precipitate flotation, ion flotation and biological processes. The removal and disposal of arsenic from metallurgical process streams will become a greater problem as minerals with much higher arsenic content are processed in the future.
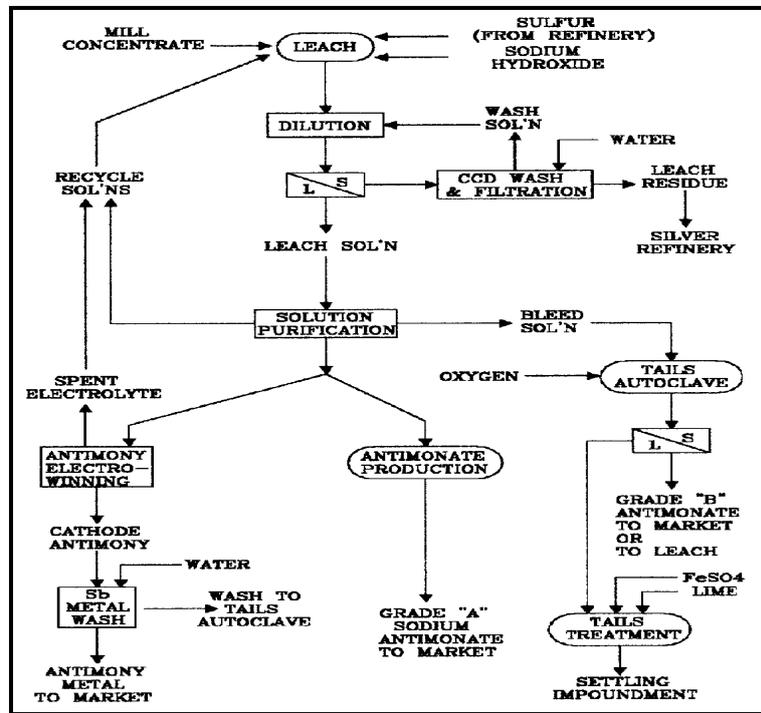

Figure 4. Historic Sunshine Mining and Refining industrial alkaline sulfide antimony metal and sodium antimonate production plant flowsheet (Anderson et al., 1992).

After smelting of sulfides or using a wholly hydrometallurgical treatment, arsenic appears in solution as either arsenic(III) or arsenic(V) but occasionally as arsenic(–III). Arsenic speciation in an uncomplexed solution is described most conveniently by means of the potential–pH diagram shown in Figure 5.
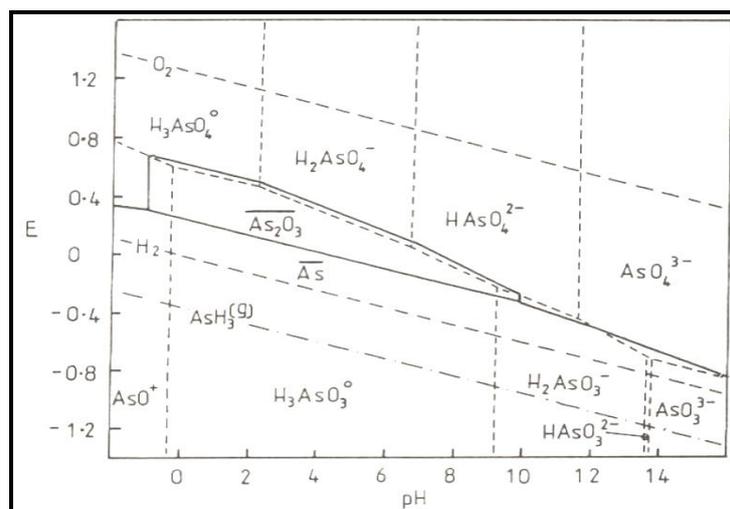

Figure 5. Eh-pH equilibrium diagram for the As-H_2O system at 25°C and unit activity of all species (Robins, 1988).

Oxidation–reduction reactions between arsenic(V) and arsenic(III) are possible using sulfur dioxide or sulfite. On an industrial scale, this process is used to precipitate arsenic trioxide from arsenic acid solutions as a commercial commodity. There appears to be little likelihood of applying more powerful reductants in hydrometallurgical processing due to the concern of producing arsine, AsH_3. Arsine gas is produced commercially, however, as an intermediate to pure arsenic metal for semiconductor use.

Arsenic Stabilization Processes

Because arsenic is most hazardous when mobile, it must be fixed as a solid precipitate to get it into a stable form for long-term storage. The two preferred stable precipitated solid forms include ferrihydrite and scorodite. Ferrihydrite is a ferric oxyhydroxide precipitate that forms very small particles with a large surface area. In treating hydrometallurgical solutions and waste streams for the removal of arsenic, the use of coprecipitation with Fe(III) has been specified by the US Environmental Protection Agency (EPA) as the Best Demonstrated Available Technology (BDAT). This technology has been widely adopted over the last century, and developments have been well reviewed (Twidwell et al., 2005). This technology has also been selected as one of the Best Available Technologies (BAT) for removing arsenic from drinking waters (Twidwell & McCloskey, 2011). Important reviews detailing conditions for formation and the stability of ferrihydrite are presented by Schwertmann and Cornell (2003), who have published a "recipe" book that presents details of how to prepare iron oxides in the laboratory, including ferrihydrite, hematite and goethite. The rate of transformation of ferrihydrite to hematite or goethite is discussed in great detail. The rate of transformation is a function of time, temperature and pH (e.g., conversion of two-line ferrihydrite to hematite at 25°C is half complete in 280 days at pH 4 but is completely converted at 100°C in four hours) (Cornell & Schwertmann, 2003). It has been pointed out by many investigators that ferrihydrite converts rapidly and that the conversion results in a significant decrease in surface area. However, the ferrihydrite conversion rate may be mitigated (changed from days to perhaps years) by the presence of other species and solution conditions during precipitation and subsequent storage (Twidwell & McCloskey, 2011). General factors that have been shown to decrease the rate of conversion of two-line ferrihydrite to more crystalline forms include lower pH, lower temperatures, presence of silicate, aluminum, arsenic, manganese, metals, sulfate and organics (Cornell & Schwertmann, 2003, 2012; Twidwell & McCloskey, 2011).

Scorodite, $FeAsO_4 \cdot 2H_2O$, is a naturally occurring mineral formed in oxidized zones of arsenic-bearing ore deposits. Its wide occurrence in comparison to other secondary arsenate minerals has led many to advocate it as an acceptable carrier for the immobilization of arsenic released during pyrometallurgical or hydrometallurgical processing of arsenic-containing ores and those of gold, copper and uranium. The production of scorodite, especially from arsenic-rich and iron-deficient sulfate solutions, offers a number of operational advantages, such as high arsenic content, stoichiometric iron demand and excellent dewatering characteristics. There are two process options of industrial relevance: the hydrothermal option that involves autoclave processing at elevated temperature (≥150˚C) and pressure and the atmospheric process based on supersaturation-controlled precipitation of scorodite at 90–95˚C. In addition to hydrothermal production of scorodite, the work done by Demopoulos (2005) has determined that it is feasible to produce scorodite by step-wise lime neutralization at 90°C. The atmospheric scorodite possesses the same structural and solubility characteristics with the hydrothermally produced scorodite. Thermodynamic calculations determined that scorodite is stable in the presence of ferrihydrite under oxic conditions up to pH 6.75 at 22°C or higher pH at lower temperature and gypsum-saturated solutions. Crystalline scorodite has been prepared many ways. Dove and Rimstidt (1985) prepared scorodite by mixing ferric chloride and sodium arsenate solutions and equilibrating the resultant slurry for two weeks at ~100°C.

Stability of Arsenic-Bearing Residues

A review of methods for the environmentally acceptable disposal of arsenic-bearing residues, such as those produced from hydrometallurgical operations, indicated that chemical precipitation as a metal arsenate offered the best solution, not only of precipitating arsenic from process liquors, but also of producing a residue sufficiently stable (giving <5 mg As/L in solution) for disposal. Since published

thermodynamic data suggested that metal arsenates were not as stable as had previously been thought, the Noranda Research Centre undertook a comprehensive laboratory study of the stability of metal arsenates, such as might be precipitated from typical hydrometallurgical process solutions, as a function of time and pH. The results indicate that (i) the presence of excess ferric iron (Fe/As molar ratio >3) co-precipitated with ferric arsenate confers a high degree of stability to arsenical residue at pH ≤7, (ii) the presence of small quantities of base metals (Zn, Cu, Cd) in solution, in addition to excess ferric iron, at the time of precipitation confers stability on the residue in the pH range 4–10, and (iii) naturally occurring crystalline ferric arsenate (scorodite) has a solubility some two orders of magnitude lower than the chemically precipitated amorphous form (Harris & Monette, 1988).

ENARGITE CONCENTRATE ALKALINE SULFIDE TREATMENT

In practice, the antimony, arsenic and some gold and silver are leached in the ASL process. Liquid–solid separations are carried out using both thickeners and media filters. The gold in solution is recovered to a final activated carbon product amenable to a common activated carbon adsorption desorption recovery circuit. The antimony is then processed to an oxide of superior quality. This was done using industrial hydrometallurgical oxidation followed by purification. Finally, the arsenic in solution is precipitated with iron salts to produce a stabilized solid. All of these unit operations for Au, Sb and As separation and treatment have been carried out successfully in industrial operations. Figure 6 illustrates a proposed flowsheet for a South American copper enargite concentrate treatment.

Figure 6. Proposed modern ASL flowsheet for copper enargite concentrate treatment.

As shown in reaction 16, the arsenic from enargite selectively dissolves arsenic into solution as a soluble salt. Table III lists the elemental composition of a commercially available enargite concentrate while Figure 7 is an example of an automated mineralogy image of that concentrate. This concentrate was tested with industrial ASL technology and the laboratory results were optimized using *Stat Ease* software.

$$2Cu_3AsS_4 \text{ (s)} + 3Na_2S \text{ (aq)} \rightarrow 3Cu_2S \text{ (s)} + 2Na_3AsS_4 \text{ (aq)} \qquad [16]$$

Table III. Industrial enargite concentrate elemental composition and mineralogy.

Elemental composition by ICP and FA*		QEMSCAN mineralogy	
Cu (%)	20.64	Pyrite (%)	54.2
Fe (%)	28.3	Enargite (%)	30.4
As (%)	5.89	Cu/As/Sb group (%)	4.78
Ag (g/t)	51.6	Covellite (%)	4.18
Au (g/t)	1.93	Copper clays (%)	1.96
Sb (g/t)	678	Bornite (%)	1.45

* Inductively coupled plasma optical emission spectroscopy and fire assay
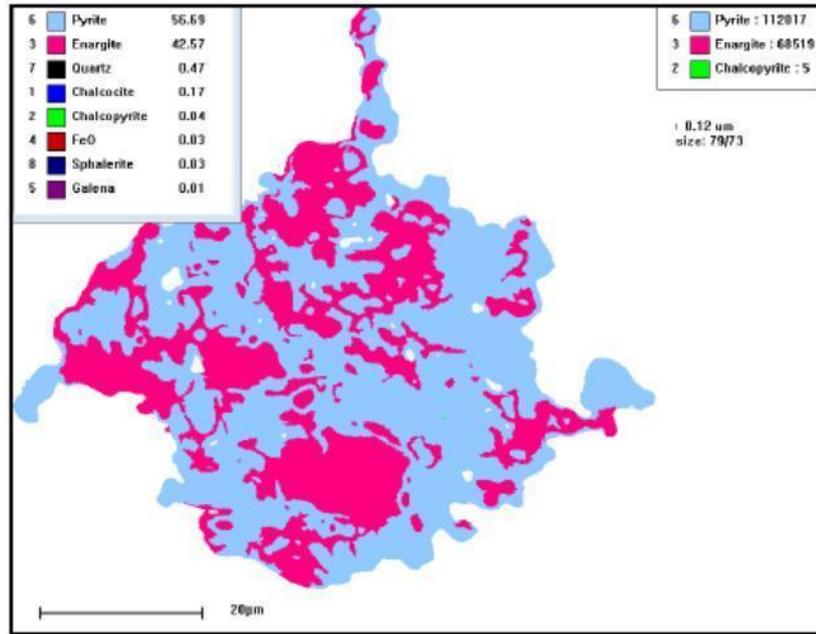
Figure 7. MLA analysis of major phases present in a particle of enargite concentrate.

Based on the laboratory results, *Stat Ease*-optimized computer models produced the following fitted equations:

As: $\sqrt{[As]}$ = 1.11 – 0.075 (time) – 0.34 (temperature) + 0.18 (solids) – 0.22 [OH⁻] – 0.71 [S⁻²]   [17]

Sb: log([Sb]) = 2.06 – 0.038 (time) – 0.23 (temperature) + 0.14 (solids) – 0.16 [OH⁻] – 0.45 [S⁻²]   [18]

Au: [Au] = 1.66 + 0.12 (time) + 0.081 (temperature) – 0.019 (solids) + 0.019 [OH⁻] – 0.13 [S⁻²]   [19]

Ag: [Ag] = 55.28 + 0.94 (time) + 0.94 (temperature) – 0.27 (solids) + 0.23 [OH⁻] + 0.31 [S⁻²]   [20]

Figure 8 shows an example of a *Stat Ease*-optimized response surface image generated in the study.
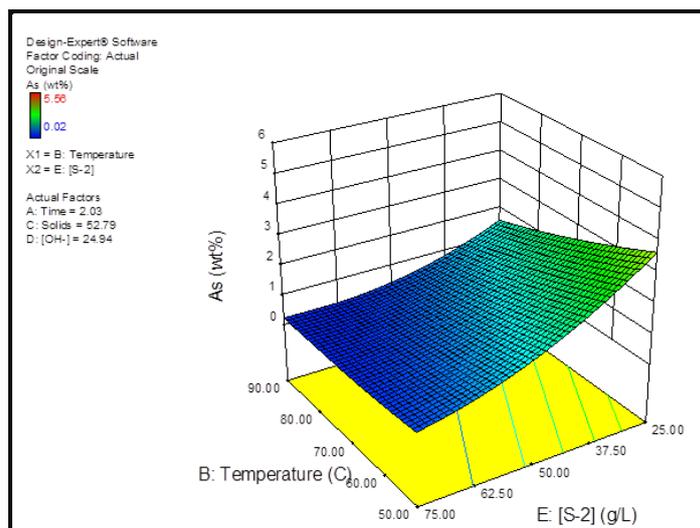
Figure 8. Enargite concentrate arsenic content leaching response at optimal conditions.

The optimized open cycle leach conditions were found to be a 2 hour leach time at 90°C with 57 g/L solids, 24.7 g/L OH- and 68.8 g/L S²- concentrations. This resulted in a 16% concentrate weight reduction with very selective and high removal of As and Sb, along with some Ag and Au lixiviation. No copper or iron were leached. For reference, Table IV lists the qualitative and quantitative analysis of the optimized ASL-treated enargite concentrate, with the appearance of a chalcocite phase and the complete disappearance of the enargite phase noted.

Table IV. Optimized ASL-leached enargite concentrate elemental composition and mineralogy.

Elemental composition by ICP and FA*		QEMSCAN mineralogy	
Cu (%)	24.5	Pyrite (%)	64.2
Fe (%)	33.7	Enargite (%)	0.12
As (%)	0.23	Cu/As/Sb group (%)	5.98
Ag (g/t)	56.0	Covellite (%)	4.92
Au (g/t)	1.58	Copper clays (%)	2.31
Sb (g/t)	23.3	Bornite (%)	2.01

From the noted optimization responses, a preliminary process was designed. Economic analysis was performed based on plant design and operating conditions formulated in the design criteria. Capital expenses (CAPEX) and operating expenses (OPEX) were calculated based on industrial experience. Further, the design was evaluated for a 15-year life on a before-tax basis. The CAPEX calculation came to just under USD 49 million (±35%). At 400 dry t/d of enargite concentrate processed, the operating expense came out to approximately USD 32 million per year. The highest cost of operation is reagents, which could be lowered with further optimization, recycle and the inclusion of reagent regeneration.

For reference, a typical industrial copper smelter penalty listing is shown in Table 6, which was used in the economic evaluation. The final estimated economic value comes out to a savings of USD 97 million per year or USD 665/t concentrate processed. This takes into account the reduction in arsenic content, the reduction in enargite concentrate weight, the sale of a high-purity antimony by product and the direct sale of the leached gold and silver loaded onto carbon. The concentrate weight reduction contribution of about 16 % after arsenic removal reduces costs in two ways: it saves shipping costs to the smelter and increases the copper and other concentrations in the final solids (which gives more favourable prices from the smelter). These values result in a total savings of USD 1.23/lb copper. This is a significant savings for a product that currently sells now for about USD 3/lb.

Table 6. Typical copper smelter penalty element costs.

Penalty element	Limit (dry metric tons)	Penalty cost
As	0.10%	USD 5.00/0.1% (up to 0.5% As)
		USD 11.00/0.1% (>0.5% As)
Bi	200 ppm	USD 4.00/100 ppm (up to 1200 ppm Bi)
		USD 6.00/100 ppm (>1200 ppm Bi)
Se	0.05%	USD 5.00/0.01% Se
Sb	0.10%	USD 4.00/0.1% Sb
Cd	200 ppm	USD 4.00/100 ppm Cd
Pb	1%	USD 2.75/0.5% Pb

The yearly expenses and savings were used to determine various economic evaluations. Over an assumed 15-year project life, the project is expected to have an internal rate of return (IRR) of 132%, a net present value (NPV_8) of USD 505 million and a present value ratio (PVR) of 10.4. Payback for this investment is just over nine months. A sensitivity analysis was performed for changes in NPV and IRR. Figure 9 clearly shows that the project is robust, with up to 20% changes in the discount rate, OPEX and CAPEX.
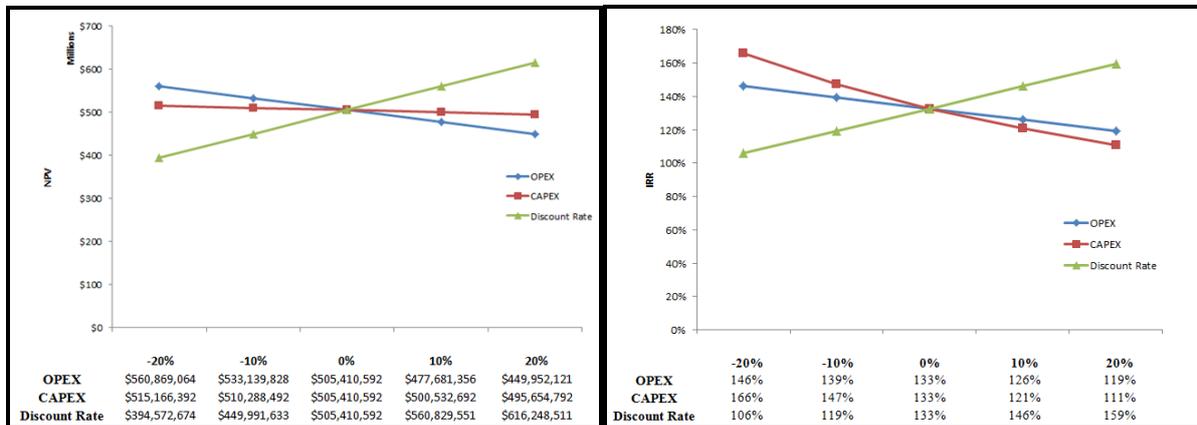

	-20%	-10%	0%	10%	20%
OPEX	$560,869,064	$533,139,828	$505,410,592	$477,681,356	$449,952,121
CAPEX	$515,166,392	$510,288,492	$505,410,592	$500,532,692	$495,654,792
Discount Rate	$394,572,674	$449,991,633	$505,410,592	$560,829,551	$616,248,511

	-20%	-10%	0%	10%	20%
OPEX	146%	139%	133%	126%	119%
CAPEX	166%	147%	133%	121%	111%
Discount Rate	106%	119%	133%	146%	159%

Figure 9. ASL enargite process NPV and IRR sensitivity analysis.

SUMMARY

This paper has illustrated the fundamentals of industrial alkaline sulfide leaching (ASL) technology. A modern example of the technology used to effectively treat copper enargite concentrates, along with the perceived site specific economics, is illustrated. In conclusion, ASL is a proven, selective industrial hydrometallurgical technology that has improved dramatically over 60 years of operation since the early 1940s when it was first practiced effectively at Sunshine Mining and Refining Company in Kellogg, Idaho, USA.

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