SCORODITE IN THE CESL PROCESS FOR COPPER-ARSENIC CONCENTRATES

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ABSTRACT

The proportion of arsenic-bearing copper concentrates that supply the copper industry is on the increase. The current strategy of miners and smelters to blend feeds to reduce average arsenic levels is rapidly becoming unsustainable as more concentrates with even higher arsenic levels enter the marketplace. In addition, the capability of smelters to manage increasing arsenic levels to more stringent and restrictive environmental standards is limited by available process technologies.

CESL Cu-As Technology is a viable technical and economic alternative to traditional smelting. It offers the advantage of simultaneous leaching and precipitation of the arsenic in a single processing step while achieving high copper extractions. The process has been piloted in six separate, fully-integrated pilot campaigns for feeds ranging from ~1% to 12% arsenic in concentration. This paper will focus on the behaviour of arsenic in CESL's leaching/precipitation step and operational factors that influence it, and on the chemical and physical characteristics of the subsequent iron-arsenic residue that represents today's best available technology from a long-term sustainable (capital/operating costs, metal recovery, safety, environmental) perspective.

The examples provided will demonstrate copper extractions approaching 99% and arsenic deportment to residue of 99%. Instantaneous settling rates of the residue were measured at 15+ m/hr. Data from subsequent short and long-term stability testing of the residue confidently support the view that the scorodite-bearing residues from the process will be stable and provide an acceptable arsenic management practice. The technology offers increased revenue and environmental certainty for miners, smelters & refiners to support the development of metallurgically challenged copper-arsenic deposits. Furthermore, results will be presented demonstrating the technology's ability to successfully incorporate hazardous arsenic containing smelter by-products such as dust into the process feed and simultaneously extract copper value while fixing the arsenic in a stable residue.

KEYWORDS

Arsenic, scorodite, solid/liquid, copper concentrate, CESL

INTRODUCTION

There are important flowsheet implications for hydrometallurgical processes that treat feeds with appreciable levels of arsenic. Processes that rely on high pH or basic leaching conditions are left with solubilized arsenic, where iron is absent, that must subsequently be fixed in an environmentally sound manner. Processes that operate under acidic conditions have the opportunity to co-precipitate the arsenic along with the iron that is being leached. Since arsenic precipitation with iron removal can be incorporated into a single leaching step, this is seen as advantageous.

Various compounds can be precipitated under hydrothermal conditions (>100ºC) when iron and arsenic are found in solution. Swash and Monhemius (1998) reported most of these minerals as shown in Table 1.

Table 1 – Major iron and arsenic mineralogical components precipitated under hydrothermal conditions

Mineral		Ideal Formula
Hematite		Fe_2O_3
Basic Iron Sulphate	(BFS)	$Fe(SO_4)(OH)$
Jarosite		$H_3OFe_3(SO_4)_2(OH)_6$
Scorodite		$FeAsO_4.2H_2O$
Ferric Arsenate sub-Hydrate	(FAsH or Type 1 (Phase 4))	$Fe(AsO_4)(H_2O)_{0.75}$
(Basic) Ferric Arsenate Sulphate	(BFAS or Type 2 (Phase 3))	$Fe_2(AsO_4)(SO_4)(OH).nH_2O$

In an iron only system, hematite is favored at 150 ºC when solution acidity is low, jarosite at higher acid levels, while basic iron sulphates tend to dominate at higher temperatures and acidities (Fleming, 2009).

When arsenic is present, scorodite is the dominant phase to precipitate at 150ºC (Gomez et al., 2011) which is the temperature of greatest interest in the present paper. The precipitate is not ideal containing about 1% S in its lattice depending upon initial conditions (Fujita et al., 2012). The finding is consistent with that of other investigators as summarized by Gomez et al. (2008) which is suggestive of minor, partial sulphate substitution for arsenate in the scorodite lattice. The presence of other cations such as copper in solution may cause a short-lived intermediate to form prior to crystallizing to scorodite as suggested by Gomez et al. (2011) which can result in copper and additional sulfur incorporation in the scorodite lattice. The structure of this intermediate approximates that of non-crystalline basic ferric arsenate which is normally found at higher temperature. If conditions are allowed to favor jarosite formation, arsenic incorporation approaches 1% As in sodium jarosite and 2.5% As in the potassium jarosite phase (Dutrizac et al., 1987). However, by limiting ferric levels, scorodite formation is favored. Beudantite ($PbFe_3AsO_4SO_4(OH)_6$), an analogue of jarosite, is believed to form ahead of scorodite (Escobar & Monhemius, 1988) which might make lead in feed undesirable.

The ratio of As:Fe plays an important role in scorodite formation. Not only the rate, but also the extent of arsenic precipitation, decreased with excess iron (Monhemius & Swash, 1998). Any iron in excess of the stoichiometric requirement remained in solution in their testing. As might be expected, higher acid levels led to lower amounts of arsenic precipitated. Free acidity should be kept well below 60 g/L (Swash & Monhemius, 1998). Time did influence the nature of the precipitate as noted above.

In an analysis of a Teck's CESL residue generated when leaching an actual concentrate, XRD analysis failed to detect an arsenic phase perhaps, in part, because the As:Fe weight ratio in feed was only 0.02 (Gomez et al., 2008). Using attenuated total reflectance infrared (ATR-IR) spectroscopy techniques, the investigators concluded that the arsenic had precipitated in a phase resembling basic ferric arsenate sulphate more so than scorodite despite the 150ºC operating temperature.

Subsequent mineralogical analysis of CESL residues produced in the pilot plant demonstrated that the arsenic was precipitated as Type II scorodite ferric arsenate (Bruce et al., 2012).

Only scorodite and basic ferric arsenate sulphate easily pass the standard TCLP test for dissolved arsenic (Gomez et al., 2008) implying the possible existence of two stable forms of iron-arsenic precipitate. Longer term tests, approaching 300 days, indicated continuing stability of these two phases. The phases showed similar leaching characteristics over time, but maintaining a low pH environment was important to both (Gomez et al., 2011). Blending of these types of residues with high pH tailings would therefore appear to be unwise as a long term storage strategy. Swash & Monhemius (1998) pointed out that scorodite, unlike other iron arsenates, is to be found in many climates around the world within a wide range of geological environments, and that this provides compelling evidence for its long term stability.

With CESL Cu-As Technology (operated at 150ºC), the precipitation of arsenic, while dissolving copper from concentrate feed, occurs under conditions that differ somewhat from the idealized studies referred to above. Instantaneous ferric and arsenic solution levels may be lower because leaching and precipitation occur simultaneously. Free acid is also perhaps lower because it is consumed in some of the leaching reactions. Impurities are introduced to the leach solutions at varying concentrations, particularly when operating fully integrated, continuous circuits. Materials providing potential seed surfaces for precipitation can also be varied. The resulting iron-arsenic residues are therefore more complex and their characteristics are the principal topic of this paper.

EXPERIMENTAL

CESL residues were generated in a number of continuous pilot campaigns, as well as in batch bench trials. The pilot flowsheet has been previously described elsewhere (Salomon-de-Friedberg, 2014). Throughput was typically of the order of 100 kg/day of concentrate depending upon its mineralogy which influenced the autoclave heat balance. Closed circuit operation enabled impurity concentrations to reach steady state.

Batch testing was performed in a 2 L titanium Parr autoclave. Concentrates were mixed with acidic, chloride and copper containing feed liquor to a slurry volume of 1.1 L and heated to 150 ºC at which point oxygen was introduced. Total vessel pressure was usually kept 14.5 bar. A bleed ensured that oxygen in the gas space was maintained at a minimum of 80% O_2. The reaction was allowed to proceed for a predetermined length of time which was normally 90 minutes.

Slurry discharge samples were filtered and washed with the residue dried at 60 ºC overnight prior to assaying. Both solids and filtrate were assayed by ICP-OES (inductively couple plasma optical emission spectrometry). Solids had first been digested in aqua regia. The higher copper levels in filtrates were titrated using recognized methods.

Residues were characterized by the following ways: chemical composition, solid-liquid separation characteristics, XRD patterns, behavior under TCLP conditions and, behaviour in long term stability tests.

RESULTS

Fe & As Precipitation during Leaching

Maximizing arsenic precipitation within the CESL autoclave operating at 150ºC is considered advantageous to generate a stable residue. Principal factors influencing the extent of arsenic precipitation were believed to be acidity of the leach filtrate and the arsenic to iron ratio fed to the autoclave as noted by Monhemius & Swash (1999). In the present work, a better correlation was found to exist between the fraction of arsenic dissolved in filtrate and the expression "free acid equivalent". This is defined as the acid titrated in filtrate plus acid that would have been generated had the soluble iron present precipitated to form acid. The corresponding relationship for a set of a different concentrates (ranging in concentration from 7% to 13% As) is given in Figure 1.
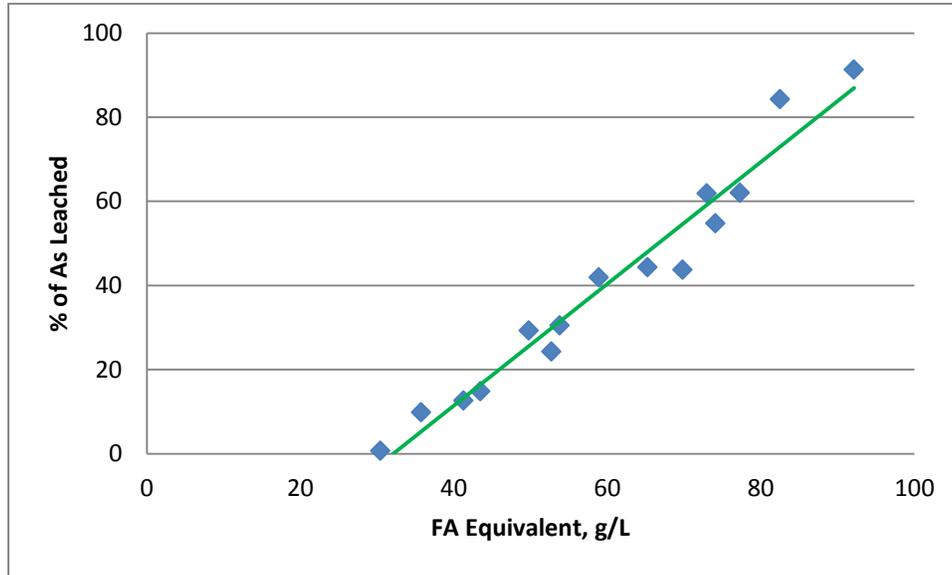
Figure 1 – Arsenic leaching from concentrate versus "Free Acid Equivalent"

This relationship indicates that arsenic in filtrate can be minimized by restricting the acid and iron in feed solution and by limiting acid generating species, particularly pyrite, in the feed concentrate. Minimizing sulphur oxidation in the autoclave is also beneficial from a capital and operating cost perspective.

For a given concentrate, the fraction of solubilized arsenic correlated closely with the final iron in leach filtrate (Figure 2).
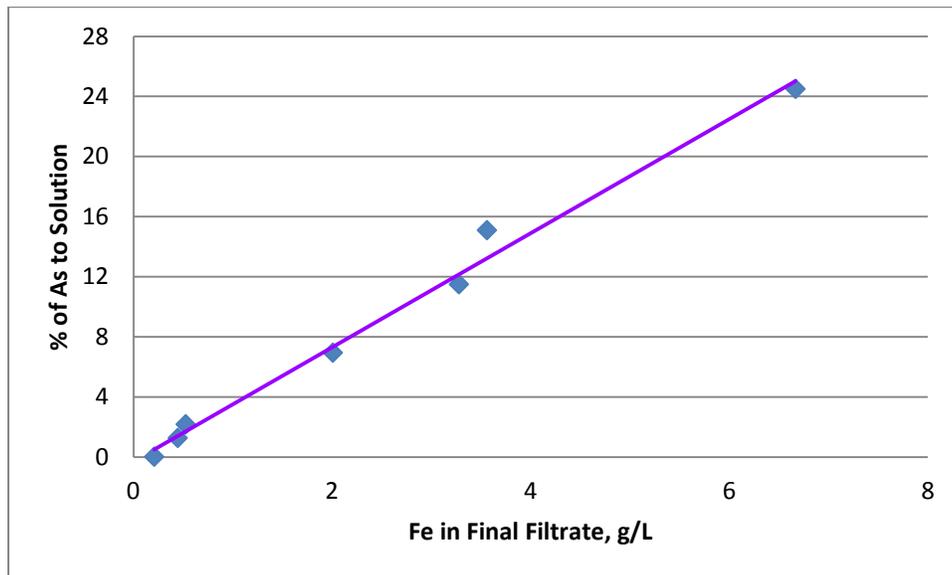

Figure 2 – Dissolved arsenic versus remaining iron in solution

No clear relationship was seen, among a dozen concentrates, between the As:Fe weight ratio in the concentrate and the fraction of arsenic reporting to solution for a given level of final acidity. The type of surfactant used in the leach and the salt content of the leach solution affected arsenic deportment only

marginally. Higher oxygen partial pressure and higher temperatures favored more complete oxidation as reflected by the higher final oxidation-reduction values and greater extents of arsenic precipitation.

In continuous pilot runs the relationship between arsenic in autoclave filtrate and free acid equivalent was similar although the slope and intercept were somewhat different (Figure 3). For the five campaigns shown, the data sets all form a similar pattern to that seen in batch testwork despite the wide range of arsenic in feeds (0.7 to 4.4% As) and fluctuating operating conditions across these campaigns.
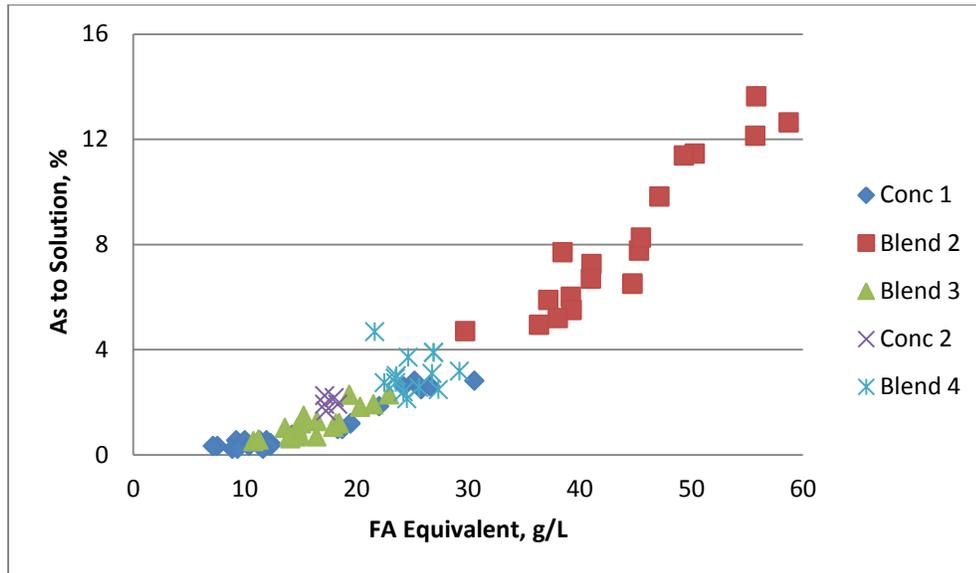

Figure 3 – Continuous operation showing fraction of arsenic left in solution as a function of FA equivalent

Copper Leaching

Batch tests demonstrated copper extraction in some cases approaching 99% for concentrates covering a broad range of arsenic compositions (Table 2). Arsenic in feed did not correlate strongly with copper extraction.

Table 2 – Copper extraction from concentrates with varying arsenic contents

Concentrate	As Content, %	Cu Extraction, %	Cu in Residue, %	Cu as S= in Residue, %
A	0.43	98.5	0.55	0.05
B	0.67	98.3	0.5	0.1
C	0.75	97.7	1.0	0.1
D	0.92	98.9	0.55	0.2
E	2.4	98.7	0.6	0.2
F	3	98.4	1.0	0.1
G	4.8	98.3	1.2	0.2
H	9.7	98.6	1.0	0.6
H-2	10	98.6	1.0	0.7

The unreacted residual copper sulphide component (mostly enargite) in residue varied from one concentrate to another indicating that the reactivity of a mineral for a given set of conditions is not simply a function of its chemical composition. The remaining portion of unrecovered copper is present in an

oxidized form that is adsorbed onto the residue surfaces as well as incorporated within the structure of that residue. The copper oxide portion can be variable (0.3 to 1% Cu) and is largely associated with minor amorphous iron phases in the residues (Sahu & Asselin, 2011).

As-Bearing Dust Additions

Copper smelters produce impurity-laden, copper bearing dusts with significant levels of arsenic which must be bled from their circuits to properly manage circuit chemistry. The addition of such dusts to the CESL autoclave offers an opportunity to leach the copper contained in these dusts while precipitating the arsenic in a stable form.

A series of standard bench tests was performed with a blend of smelter dust and concentrate, with the composition of materials as presented in Table 3.

Table 3 – Composition of concentrate and dust fed to bench leach

Material	As, %	Cu, %	Fe, %	S, %
Concentrate	2.19	31	19	35
Dust	10.5	19.3	13.4	8.3

Arsenic bearing dust additions were 0, 10, 20, and 30% by weight of the input concentrate which was kept unchanged at a 100 g/L solids density. With increasing dust charge, the fraction of arsenic reporting to filtrate fell from 1.8% or 0.042 g/L As (no dust addition) to 0.5% or 0.026 g/L As (30% dust addition) despite the steadily increasing arsenic feed grade.

Copper extraction from only the concentrate was 98.5%. Cu extraction from dust was 88 to 89% and was unaffected by the quantity of dust on charge. Consequently, overall Cu extraction slipped slightly with increasing dust levels as shown in Figure 4.
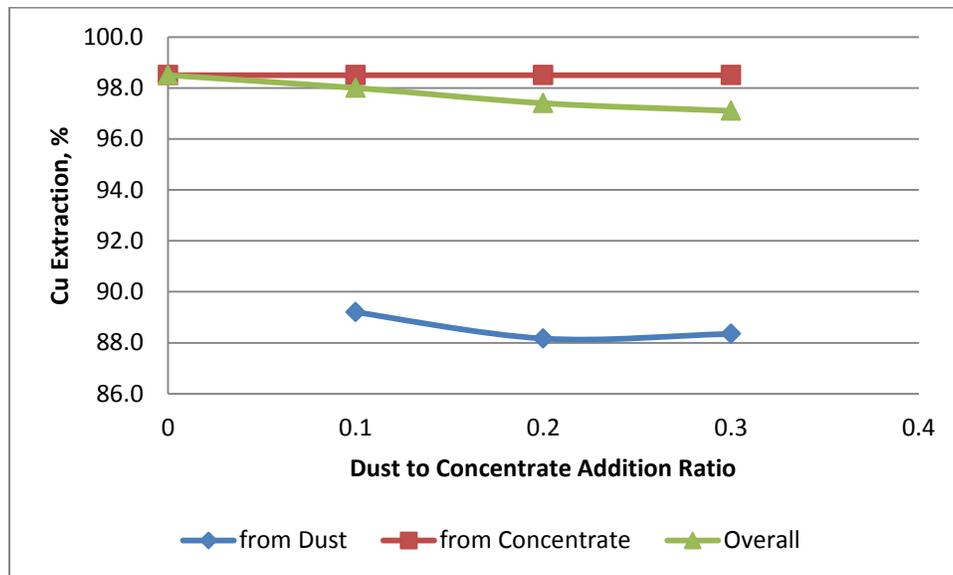

Figure 4 – CESL copper extraction from smelter dust and concentrate blend

The addition of dust to an autoclave operating under standard CESL conditions offers the benefit of increased throughput for the vessel, as it has little impact on the operating heat balance, with no adverse impact on arsenic deportment.

Chemical and Physical Residue Characterization

Mineralogical Characteristics

Mineralogical analysis of residues produced in the continuous, fully integrated CESL pilot plant demonstrated that the arsenic was precipitated as Type II scorodite ferric arsenate, widely accepted as the best available technology for stabilizing arsenic (Ferron & Wang, 2003). A previous paper discussed the different forms of ferric arsenate precipitated depending on autoclave and operating conditions (Bruce et al., 2012).

Since the prior publication, additional quantitative X-ray diffraction analysis has been completed on processing smelter dusts under CESL conditions through bench testing. The results of quantitative phase analysis by Rietveld refinements are given in Table 4. This data represent the relative amounts of crystalline phases normalized to 100%. It is estimated the sample contains, in total, 30% amorphous material.

Table 4 – Quantitative X-ray diffraction analysis of CESL residue produced from smelter dust feed

Mineral	Ideal Formula	Weight, %
Quartz	SiO_2	18
Scorodite	$Fe^{3+}AsO_4.2H_2O$	23
Sulfur	S	13
Hematite	$\alpha\text{-}Fe_2O_3$	3
Maghemite	$\gamma\text{-}Fe_2O_3$	30
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	5
Illite/Muscovite 2M1	$\sim K_{0.65}Al_{2.0}Al_{0.65}Si_{3.35}O_{10}(OH)_2$	7
Famatinite	Cu_3SbS_4	1

Physical Characteristics

The formation of residues that exhibit good solid-liquid separation characteristics is a fundamental requirement of a hydrometallurgical process. A previous paper published settling data from residues produced under standard CESL conditions (Defreyne et al., 2006). These residues were principally hematite and elemental sulphur, and contained negligible arsenic.

On CESL residues that contained 16% arsenic with principally a Type II scorodite and elemental sulphur composition, excellent settling characteristics were achieved as shown in Table 5.

Table 5 – Settling results on pilot plant (scorodite) residue

Criteria	CCD
Instantaneous settling rate, m/h	15.5
Unit area, m^2/tpd	0.15
Overflow solids, ppm	50
Underflow solids, wt%	50
Residue P80, μm	46

The scorodite bearing residue exhibits similar settling characteristics as achieved with hematite, which eliminates engineering concerns as compared to poorer settling residues that contain significant jarosite or basic iron hydroxides.

Stability Assessment

Pilot residues, produced during past pilot campaigns, containing up to 16% arsenic were subjected to the Environmental Protection Agency's (EPA) standard hazardous material characterization procedure

(TCLP, Method 113). The consistently low arsenic in the tests (~0.05-0.1 mg/L) versus the EPA limit of 5 mg/L demonstrated that the residues were non-hazardous (Lossin et al., 2015).

Assessment of these non-hazardous residues over a longer time period was equally important. A number of residue samples from previous high arsenic pilot plant campaigns were placed in two-liter bottles with residue at a 20:1 liquid to solid ratio. These are being monitored on an ongoing basis while subjected to mild agitation at room temperature. The equipment used is an orbital shaker (Lab-Line Instruments Orbit Shaker, No. 3590) at 100-110 rpm and 2 cm lateral motion. Results are shown in Figure 5, with residue stability results supporting earlier findings (Gomez et al., 2008) that scorodite and basic ferric arsenate sulphate easily pass the standard TCLP test and longer term geochemical tests, implying the existence of two stable forms of iron-arsenic precipitate.
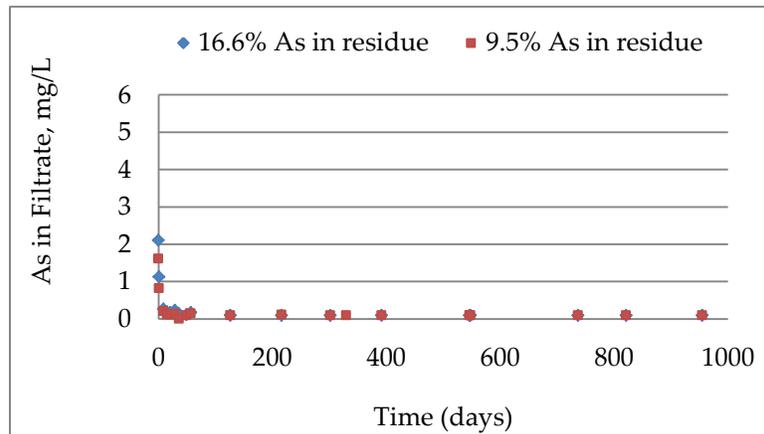

Figure 5 – Long-term residue stability results

INDUSTRIAL APPLICATION

Hydrometallurgical processing of copper concentrates containing elevated levels of arsenic represents the best available option to address environmental implications of produced arsenic residues inherent to the production of copper using complex feed materials. Successful commercialization also requires the technology to meet minimum economic hurdles. The CESL Cu-As Technology has demonstrated its ability to provide a sustainable solution that deals with contained arsenic in an environmentally sound manner, while minimizing the complexity and cost of processing by containing the copper leaching and arsenic precipitation reactions within a single step. Furthermore, settling of the arsenic-containing residue has eliminated engineering concerns, providing further certainty as to the economic viability of the process.

Long-term increasing demand of copper is estimated to require the development of an additional five million annual tonnes of copper capacity from new mine production during the period of 2014 – 2024 (Wood Mackenzie, 2015). Increasing impurity levels in concentrates, e.g. arsenic level, is predicted. Declining head grades combined with higher investment and operational cost will require the reassessment of copper deposits, including those with high arsenic grade, which have been undeveloped so far. China has restricted copper concentrate import at 0.5% arsenic content. The Chinese import ban is an indication of the copper concentrate processing industry's current inability to safely and cost effectively handle high arsenic materials. Typically such high arsenic bearing concentrates are blended with clean concentrates to meet legislative and technical thresholds. The practice of blending is limited by available volume of clean concentrates and the increased costs and logistics of performing the blending. While blending may solve the issue of technical threshold requirements for current copper refining technologies, it does not address the burden that the produced unstable arsenic waste materials place on the environment, nor does it represent a sustainable solution (Drouven, 2015).

Conceptual case studies have been conducted to assess the business case for a commercial CESL Cu-As Technology installation. A copper price of 2 $/lb has been shown as break even for a greenfield mine to metal project with 200 ktpa copper production and 1.5% arsenic content in concentrate (Salomon-de-Friedberg et al., 2014). A further opportunity for improving the economics is the integration of a CESL Cu-As pressure leach operation into an existing copper SX/EW circuit with excess underutilized capacity, as is common for operations with undeveloped hypogene sulphide deposits that underlie late stage copper heap leaching operations. Due to low arsenic concentration in the PLS, the excess sulfuric acid could be utilized for the existing heap leaching operations at the nearby facility, with enhanced economic results.

After 5 years of successful technical development of the CESL Cu-As Technology, Teck and Aurubis have established it as a sustainable technology. Moving forward, they intend to demonstrate the technical and economical capability of this technology in a full scale CESL Cu-As production plant in South America.

CONCLUSIONS

The processing of high arsenic bearing copper concentrates at levels of up to 12% arsenic has been successfully demonstrated in continuous, fully integrated pilot campaigns. Copper extractions in excess of 97% were achieved from concentrates containing chiefly enargite. Arsenic was effectively captured in an iron residue during the same copper leaching step.

Testing at both the bench and pilot scale has demonstrated arsenic deportment to the residue is a function of both the autoclave discharge iron and free acid tenors. Maximizing arsenic deportment to the stable residue is important from both an economic and sustainability perspective. Furthermore, the CESL Cu-As Technology has demonstrated scorodite production when processing smelter dusts which contain iron and arsenic.

Residues from these trials all passed the EPA TCLP regulation that would qualify them as a non-hazardous waste. Long term stability testing over a period exceeding 3 years has shown no tendency for arsenic leaching to increase from residues containing up to 16% arsenic. These tests continue.

Moving forward Teck and Aurubis are evaluating the commercialization of the technically proven CESL Cu-As Technology. The technology provides favorable economics for high-arsenic ores, particularly if the location has a heap leach operation with available SX/EW capacity.

ACKNOWLEDGMENTS

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