Hydrometallurgical considerations in processing arsenic-rich copper concentrates

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ABSTRACT

It is projected that, with steadily increasing arsenic levels in copper concentrates, the world-wide copper smelter capacity for arsenic will soon be exceeded, severely impacting blending as a viable solution to unlocking the value of copper and precious metals (gold, silver) from high arsenic-bearing deposits. New copper recovery technologies that provide sustainable, long term arsenic capture and containment are essential if copper deposits with elevated arsenic levels are to be responsibly developed.

This paper reviews recent results from both bench and integrated pilot scale testwork performed with copper concentrates containing from 1% to 10% arsenic. The application of medium temperature pressure leaching, in this case CESL Cu-As Technology, is assessed in several key areas: copper extraction, silver and gold recovery from leach residue, arsenic capture to residue within the leaching vessel, and, particularly, stability of the final residue. Optimal copper extraction results exceeded 98% in bench work with parallel Pilot results achieving >97% copper recovery to LME Grade A cathode over extended, fully integrated, test campaigns. Bench pressure cyanidation of the copper pilot residues confirmed that up to 90% silver extraction was feasible, with extractions being sensitive to the upstream copper leaching conditions. Arsenic precipitation within the leaching vessel in most cases was >97% and the factors influencing final arsenic in the leach filtrate are presented. All final residues easily met the toxicity characteristic leaching procedure (TCLP) arsenic limit of the USA Environmental Protection Agency (EPA). The suitability of the technology in today's regulatory environment is also discussed.

INTRODUCTION

Increasing arsenic in copper concentrates has been a concern in the mining industry for decades as evidenced by organized symposia on the topic (CIM/COM, 2014; TMS 2005; TMS-AIME, 1988). The amount of arsenic which can be processed by smelters is constrained by technical limitations and ever tightening environmental, health and safety restrictions. Moreover, a recent ban on importing copper concentrates with arsenic levels exceeding 0.5% into China is encouraging further processing of these materials in the countries of their origin.

A number of ore deposits that previously had produced "clean" concentrates are now generating concentrates with higher impurities as they move into more complex regions of the orebodies. In addition, several new, severely arsenic-challenged deposits have come into production. Two out of four greenfield copper mining projects, which started production during 2014, produced concentrates that contain arsenic levels in excess of 1% - Mina Ministro Hales and Toromocho where selective mining and ore stockpiling were needed to reduce the arsenic level in concentrate. CRU reports there are several other arsenic-bearing copper deposits, which are expected to replenish the primary copper raw material supply – Canariaco Norte, Altar, La Granja, Zafranal, Caspiche and others (Heimlich 2015). The average level of arsenic in copper concentrates is expected to rise in the coming years and it is projected to exceed the smelters' capacity to treat it.

In order to market arsenic-bearing copper concentrates, the mining industry is resorting to selective mining and blending. When arsenic is present at high concentrations, the requirement for clean concentrates for blending purposes becomes exacerbated and the overall economics of this temporary solution become unattractive. A responsible solution for processing high-arsenic copper concentrates includes complying with future environmental standards by limiting the volume of the waste and converting arsenic to its most stable form for safe, long-term storage.

Over the last five years, Teck, Canada's largest diversified resource company, and Aurubis, Europe's largest copper producer, have been jointly working on a hydrometallurgical process for treating high-arsenic copper concentrates. After testing 18 different enargite-bearing concentrates containing up to 11.8% As and running four pilot plant campaigns covering a total operating period of 12 months, the partnership has successfully developed a commercial–ready solution for processing copper concentrates with elevated arsenic content. Results from some of this testwork have been previously reported (Mayhew et al., 2011; Bruce et al., 2011; Salomon-de-Friedberg et al., 2014).

PROCESS DESCRIPTION

In any successful hydrometallurgical process treating copper-arsenic concentrates, key results would include high copper extraction during leaching and arsenic deportment to a stable residue. As most of these concentrates also contain significant levels of gold and silver, recovery of these precious metals cannot be overlooked. The CESL Cu-As Technology deals with each of these parameters effectively.

The major steps of the CESL Copper Process Flowsheet are outlined in Figure 1.
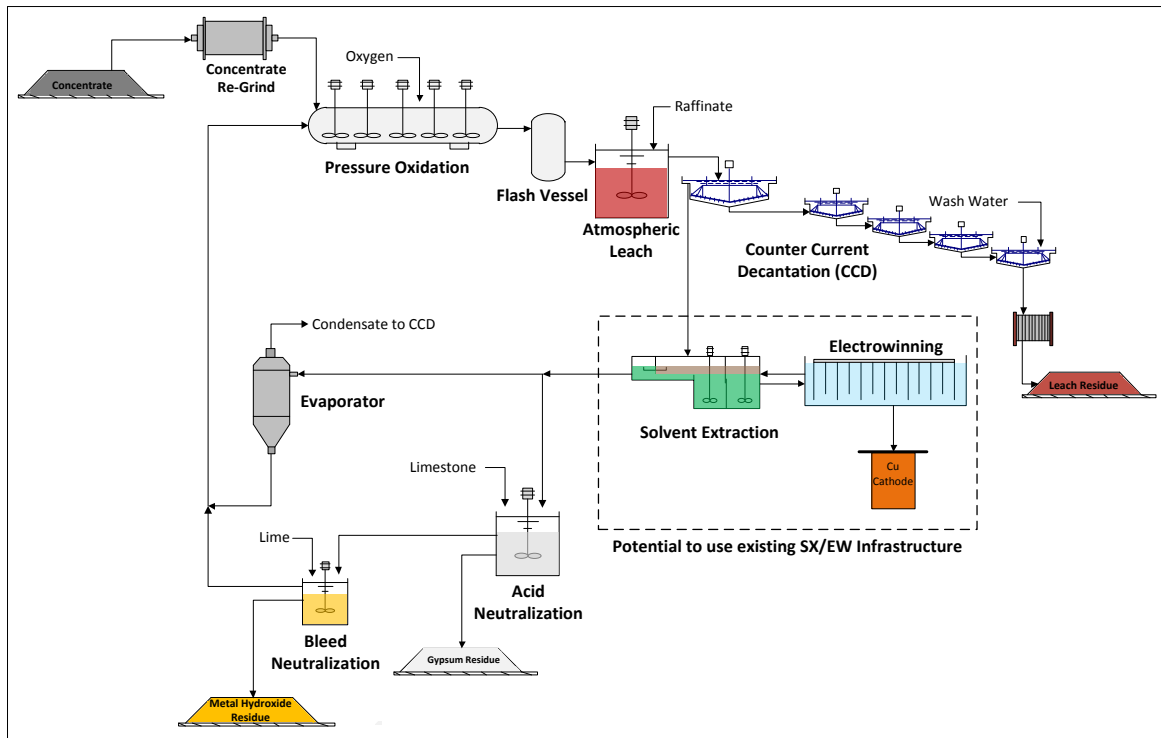
Figure 1 CESL Copper Process Flowsheet

Concentrate is first reground prior to leaching at 150°C and 14 bar pressure. Retention time in the leach vessel is in the range of 60 to 90 minutes to promote complete oxidation of the copper sulphide minerals and to maximize the extent of arsenic precipitation within the vessel. The leaching conditions favor the precipitation of arsenic as scorodite. Depending upon the slurry pH leaving the autoclave, the discharge slurry may be given a further mild leach under atmospheric conditions to further reduce the copper in residue. This is followed by a counter-current decantation circuit to wash the residues which then go to storage or further processing to recover precious metal values.

The copper-rich leach solution leaving the counter-current decantation circuit is directed to a solvent extraction and electrowinning circuit to recover the copper in cathode form as the final product. Raffinate from the SX circuit is returned to leaching. A portion may be bled at this point to supply acid to a nearby heap. Otherwise, a portion is bled to a neutralization circuit to maintain the overall sulfate balance as some of the sulphur in concentrate is oxidized to sulfate during leaching. This results in a relatively clean gypsum residue. The product solution is recycled to the main circuit except for a small portion that is treated through a Bleed SX circuit followed by lime treatment to keep minor impurity metals, such as zinc, at reasonable concentrations. The resulting metal hydroxides are waste that needs to be stored appropriately. An evaporator may be required to maintain the overall water balance for an otherwise closed circuit process, with the condensate used as wash water which lowers fresh water requirements.

Residue processing for precious metal recovery comprises the steps of: i) pressure cyanidation to minimize cyanide contact time with the elemental sulphur in residue, ii) metal adsorption onto activated carbon, followed by iii) activated carbon stripping and electrowinning to produce a

precious metal containing sludge. Cyanide bearing solutions are recycled. A bleed solution from the process undergoes residual copper recovery, and cyanide regeneration and recovery prior to being treated through cyanide destruction. Ensuring that the arsenic-bearing residues retain their long term stability characteristics after the precious metal recovery step is critical to the success of any potential process.

TECHNICAL PROGRAM

Testing was performed at two levels: bench scale, using an autoclave with a 1.1 L active slurry volume, and subsequently in a fully integrated pilot plant. The pilot autoclave active volume was 27 L with a throughput of roughly 50 kg/d of concentrate. Batch tests were used to identify the preferred operating conditions for the subsequent continuous operation in the pilot plant. The fully integrated pilot plant comprised all the unit operations of the complete flowsheet shown in Figure 1.

Earlier papers (Mayhew et al., 2011; Bruce et al., 2011; Salomon-de-Friedberg et al., 2014) reported on the application of CESL Technology to copper concentrates ranging in arsenic content from less than 1% to nearly 12%. The latest campaign dealt with concentrates having the compositions shown in Table 1.

Table 1 Composition of the latest materials processed through bench and pilot testing

Element	Concentrate "A"	Concentrate "B"
Cu, %	28	34
Fe, %	23	16
As, %	1.0	3.7
S, %	37	32
Ag, g/t	150	600
Au, g/t	1	1

The major differences in the two materials include the arsenic and silver contents. The pyrite levels were high in both concentrates ("A" ~ 43% pyrite; "B" ~ 35% pyrite). The arsenic-bearing minerals were enargite and tennantite.

In the Bench testing phase of the program, the variables assessed to increase copper extraction and promote arsenic precipitation in the autoclave included: the concentrate, grind size, acid strength of the leach solution, leach retention time, surfactant type and dosage, and other additives. Chloride level was also tested. A single bench test usually consisted of 3 components: a pressure leach, an atmospheric leach of the pressure leach residue, and a pressure cyanidation on the washed atmospheric leach residue. The first two leaches focused on copper recovery to solution and arsenic deportment to solids. The last leach was for determining silver and gold recovery from the now copper-depleted residue.

Bench Copper Extraction

Both concentrates showed a relatively tight range in copper extraction for the conditions investigated as shown in Figure 2.
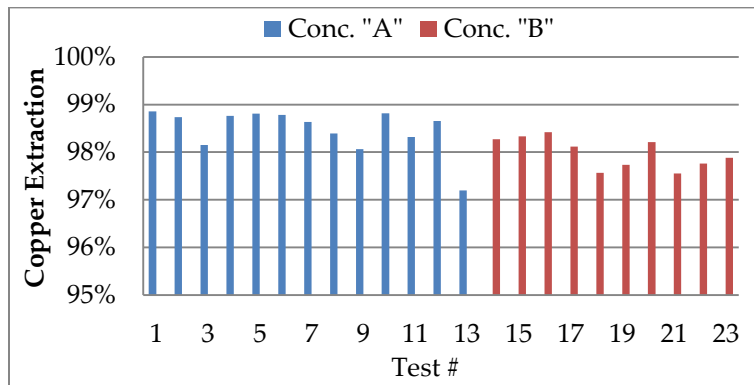
Figure 2 Range of Bench copper extractions observed for the two concentrates

Outcomes were repeatable as indicated by the repeat tests 14, 15 and 16. Concentrate "A" extractions were slightly better despite the lower head grade. The key parameter to achieving good copper extraction in the presence of chloride and surfactant was a suitable grind size (12 μm p80 for both concentrates). Copper extraction was adversely affected by high impurity (Al + K + Na) levels in solution (Test 13). Feed acid concentrations in the range tested had a minor impact. Concentrate "B", with its higher enargite content, required a longer retention time (90 versus 60 minutes) in the leach vessel.

Limiting Arsenic to Leach Filtrate

Effective arsenic precipitation in the autoclave is desirable because of the favorable conditions for making a stable residue and to limit soluble arsenic that might be diverted to heaps, for example. Arsenic deportment to leach residue is a function of many factors including As:Fe ratio in the feed materials, retention time, solids recycle, and solution acidity.

The free acid (FA) equivalent in the autoclave discharge solution was a good predictor of the fraction of arsenic left solubilized at the end of the leach. Free acid equivalent is defined as the sum of acid remaining plus any acid generated had the iron in solution precipitated. The best correlation from bench testwork performed on the two copper concentrates processed here is shown in Figure 3.
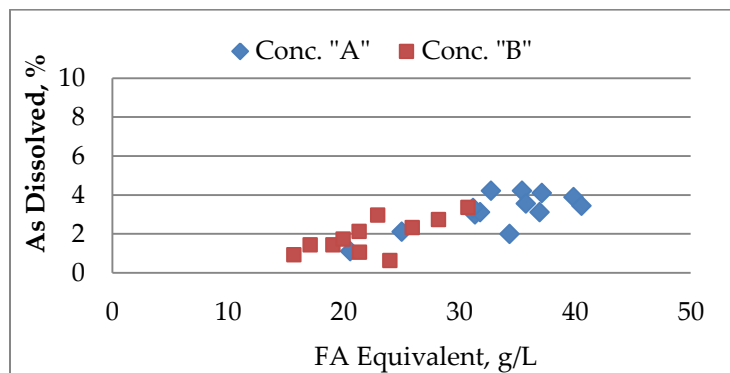
Figure 3 Arsenic deportment to filtrate versus discharge solution acidity

Aside from controlling acid tenor, greater arsenic precipitation in the autoclave was favored by higher oxygen pressure and longer retention time. These factors also helped reduce the fraction of sulphides that were left unoxidized at the end of the leach. However, filtrate Redox potential showed no correlation with the extent of arsenic precipitation observed.

Silver Extraction & Residue Stability

Silver extraction from the leach residue using CESL pressure cyanidation conditions varied considerably. Concentrate "A" achieved a maximum of 95% while Concentrate "B" was somewhat lower. The latter results were improved in the pilot plant operation as discussed later in the paper.

The most negative factors influencing silver recovery were higher acidity and total sulfate in solution in the pressure oxidation step. Shorter retention time during the pressure oxidation step favored better silver extraction.

All the residues from the pressure cyanidation step readily passed the TCLP criteria for arsenic as well as the other reportable elements thereby meeting the US EPA "non-hazardous" criteria. The arsenic values in the TCLP leachate all hovered at the detection limit (0.1 mg/L As) of the ICP-OES unit.

Pilot Program

Piloting began with Concentrate "A" for almost 3 weeks followed by Concentrate "B" which was processed for 13 days. Operations were scheduled for 5 days per week at 24 hours per day. As can be seen in Figure 4 below, initial conditions led to variable oxidation of the copper sulphide minerals.
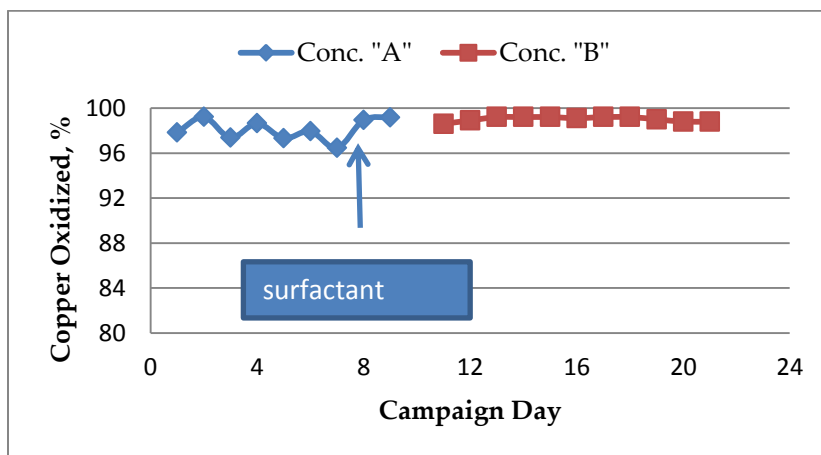

Figure 4 Oxidation of copper minerals during the two campaigns

The initial start of the campaign was less than optimal due to surfactant issues and despite an increase in surfactant concentration, the targeted oxidation levels (99%+) were not met. A change in surfactant was made after Day 8 of the first campaign and thereafter the oxidation objective was consistently realized.

The second campaign using Concentrate "B" continued with the better surfactant and achieved the desired level of copper mineral oxidation.

Previously published pilot scale testing has shown copper extractions of up to 97% can be achieved from high-enargite concentrates using CESL Cu-As Technology (Mayhew, 2011). The results achieved in this campaign when processing Concentrates "A" and "B" is an improvement from historical work, with results from the campaign presented in Table 2. The highest copper extraction results with the lower-enargite Concentrate "A" was 99.0%, with 97.8% copper extraction being achieved with the higher enargite Concentrate "B". The difference between the presented values for Cu pilot plant extraction and overall Cu extraction is the additional metal value that is recovered as a result of precious metals recovery.

Table 2 Optimal Pilot Plant Copper Extraction Results

Parameter	Unit	Conc. "A"	Conc. "B"
Cu Pilot Plant Extraction	%	98.2	97.5
Overall Pilot Plant Extraction	%	99.0	97.8

Pilot Arsenic

The net arsenic leaching in the autoclave, or delta As, averaged under 30 mg/L for the 1% As Concentrate "A" during pilot operation. For Concentrate "B", the values were higher as shown in Figure 5.
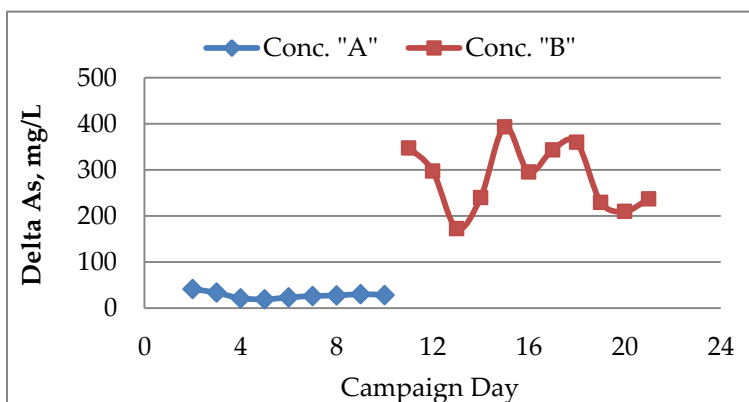

Figure 5 Arsenic dissolved across the pilot autoclave with Concentrate "A"

The average arsenic dissolved in the autoclave for Concentrate "B" was ~280 mg/L or 7.5% of the arsenic in concentrate. For the final days of this period the net arsenic dissolved approached 200 mg/L, which is believed to be due to the pilot plant approaching steady-state conditions. In comparison, a parallel bench test using pilot plant feed materials dissolved 180 mg/L As in the leach, close to the steady state value above. When synthetic (lower sulfate) feed solutions are used, the bench leach saw a net arsenic of less than under 100 mg/L in solution.

Arsenic not precipitated within the autoclave is captured in the downstream Neutralization step where it forms a non-hazardous residue as confirmed by numerous TCLP assessments that all reported arsenic values at the threshold of detection.

Pilot Silver Extraction

Previous testwork has shown that bench pressure cyanide testing of continuously produced pilot residues is a good proxy for pilot pressure cyanidation of these same residues. The silver extraction was 93% for the 1% As Concentrate "B" during pilot operation. Bench tests were carried out on Concentrate "B" residues produced in the continuous pilot plant. The benefit of adding a process reagent to the silver extraction step is shown in Figure 6, with an optimal extraction of 90%.
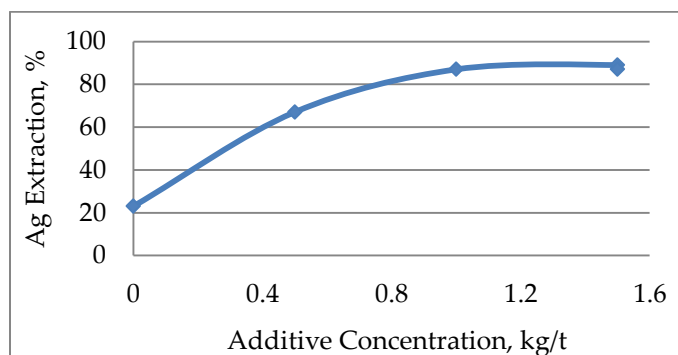
Figure 6 Benefit of a reagent addition to the pressure oxidation step

Bench pressure cyanidation when carried out on bench produced residues with no reagent addition gave a higher silver recovery of 63% (vs 23% for pilot). Again, the sulfate environment was higher for the pilot continuously generated residue. When bench tests were deliberately spiked with extra sulfate, silver extractions in the subsequent pressure cyanidation were depressed to as low as 5%.

Sulfate management in the integrated flowsheet benefits, not only silver recovery as noted above, but also favors higher copper extractions and greater arsenic precipitation in the pressure oxidation step as indicated earlier.

ALTERNATIVE TECHNOLOGIES & APPROACHES

Currently, high arsenic concentrates are being blended with clean concentrate material in order to meet the limits of smelters and import restrictions to China. The arsenic contained in copper concentrates is spread throughout the smelters and deports to large volumes of slag, dust and hazardous gypsum waste. A more sustainable solution for dealing with these arsenic-rich copper concentrates would include high payable metal extraction, competitive energy and operating costs, no gaseous emissions, and would continuously convert the arsenic into a stable form contained within a minimal amount of residue.

Hydrometallurgical research efforts are intensifying; however, more success has been achieved with chalcopyrite than with enargite concentrates. Dreisinger (2014) provides a review of the

sulfate-based hydrometallurgical technologies. Attention was focused on atmospheric leaching (Galvanox), requiring long retention times (>20h) and total oxidative leaching (TOL), with its own challenges related to economics, arsenic fixation and silver extraction.

Table 3 summarizes the major metallurgical outcomes and arsenic behavior from bench tests when processing a concentrate similar to Concentrate "B" (32% Cu, 15% Fe, 5.6% As, 30% S, 470g/t Ag) under CESL and TOL conditions. The TOL parameters were 220°C, 33atm, and 100g/L SD. Prior to cyanidation (atmospheric, in this case), the residue from TOL was subjected to a lime boil (pH 10.5 for 10hr at 95°C), in an attempt to break down the refractory jarosite species which have presumably co-precipitated Ag (also observed and reported by Dreisinger, 2014).

Table 3 Metallurgical CESL vs TOL comparison

Parameter	Unit	CESL	TOL
Cu Extraction	%	97.6	97.6
Ag Extraction	%	85	80
Sulfur Oxidation	%	57	98
Oxygen Consumption	t/t conc	0.46	0.72
Acid Generated	t/t conc	0.33	0.76
Arsenic in Autoclave Discharge	mg/L	130	400
As in TCLP	mg/L	1.7	204

Copper extraction is comparable for both processes. Using large quantities of lime for breaking up potential jarosite species formed in order to free-up silver may be technically successful, but economics will depend upon silver levels of the feed material. If the lime boil step is not applied prior to cyanidation, Ag extraction was poor (<30%), as was also observed and reported by Dreisinger (2014).

With virtually complete sulfur oxidation during TOL, the oxygen consumption and acid generation for this process were nearly twice the amount seen for CESL Technology. The additional oxygen, as well as lime required for neutralization, adds to the major reagent costs. The use of the generated acid in heap leaching may be complicated by the presence of the solubilized arsenic. Higher arsenic in the TOL autoclave discharge, equal to 12% of the total arsenic in feed, and comprising As^{+3} and As^{+5}, may influence bacterial activity in those heaps and could have long term environmental implications.

Extensive residue stability testwork at CESL indicated that, besides being an important criterion for the hazardous characterization of a material, TCLP results provide an indication of residue stability over longer periods of time. For CESL residues, this will be discussed further in the paper, whereas no data on TOL residue stability after cyanidation for this type of residue could be found.

ENVIRONMENTAL CONSIDERATIONS AND RESIDUE STABILITY

From an emissions perspective, copper smelters remain the principal sources of SO_2 and As contamination (Contreras, 2013). Only with considerable investment (~$1.500 MUS) has SO_2 capture improved in Chile from 18% to 88% but As emissions decreased by only 34% (Sanchez,

2013). A newer, more stringent 2013 regulation targets 95% capture of SO_2 and of As by 2018. In contrast, hydrometallurgical processes, being solution based, produce virtually no emissions to the atmosphere.

From an energy perspective, an on-site refinery offers the advantage of mine-to-metal production in immediate proximity to the mine. This would reduce the cost, energy and CO_2 footprint associated with shipping concentrates to distant smelters. The availability of quality water can also be a vital consideration in many parts of the world. Minimizing fresh water use and focusing on recycling and reuse has always been a focus of CESL Technology. The various water requirements of the flowsheet total ~1.6 m^3/t concentrate. The evaporator incorporated in the flowsheet ensures zero liquid effluent discharge to the environment. Recent piloting demonstrated that substitution of up to 30% of the fresh water requirements with sea water was possible (Bruce & Seaman, 2014).

Mineralogical analysis of residues produced in the continuous, fully integrated 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). Previous papers (Mayhew et al., 2011 and Bruce et al., 2012) discussed the different forms of ferric arsenate precipitated depending on autoclave and operating conditions. Pilot residues, produced during past pilot campaigns, containing up to 16% As, 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) demonstrated that the residues were non-hazardous.

Assessment of these non-hazardous residues over the longer term was equally important. A number of residue samples from previous high arsenic pilot plant campaigns were placed in two litre 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 7.
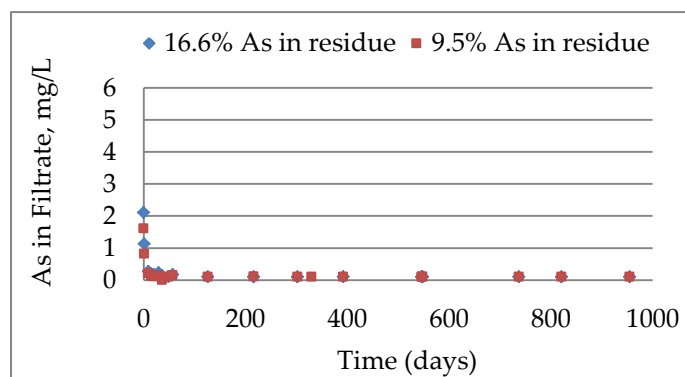

Figure 7 Long-term stability results

The results indicate that, despite the high levels of arsenic in a compact residue, the arsenic levels in solution do not increase appreciably with time (after nearly 3 years) supporting the argument that CESL derived residues represent the best alternative for a responsible process.

The occupational exposure to arsenic has also been verified to be safe. During a campaign in 2011, personal monitoring of worker' air quality and monitoring of inorganic arsenic in the urine of workers was conducted. The air quality results were all below the limit set by WorkSafe BC for exposure to arsenic during a 12-hour shift of 0.005 mg/m³. All biological monitoring samples during the Cu-As campaign were also well below the action limit of 50 μg As/g creatinine.

CONCLUSIONS

The challenge of rising levels of arsenic in copper concentrates requires the integrated mining and metals industry to pursue alternative technologies to traditional smelting. Blending to "dilute the arsenic away" is a short term and unsustainable solution.

CESL Technology has successfully demonstrated that it is capable of high copper and silver recoveries from arsenic-rich copper concentrates while recovering the arsenic as a non-hazardous stable residue. Copper extractions of up to 99% were achieved from concentrates containing significant enargite. Arsenic was effectively captured in an iron residue during the same copper leaching step. Silver was subsequently recovered (90%) from the leach residue via cyanidation. Residues from these trials all passed the US EPA TCLP regulation which qualifies them as a non-hazardous waste. Long term stability testing over a period approaching 3 years have shown no tendency for arsenic leaching from residues containing up to 16% arsenic. These tests continue.

REFERENCES

Bruce, R., Mayhew, K., Demopoulos, R., Heidel, A., (2012), Arsenic Stability and Characterization of CESL Process Residues, Conference of Metallurgists Proceedings, Niagara Falls, Canada.

Bruce, R., Seaman, T., (2014) Reducing fresh water use in the production of metals, Hydrocopper 2014, Viña del Mar, Chile.

COM 2014 – Arsenic Metallurgy & the Environment Symposium, Vancouver, Canada.

Contreras C.G., Ulloa, P., Sant, P., (2013), New Regulation to Reduce Air Emissions from Copper Smelters in Chile, Copper Conference Proceedings, Santiago, Chile.

Dreisinger D., (2014), Hydrometallurgical treatment of arsenic containing materials, Conference of Metallurgists Proceedings, Vancouver, Canada.

Ferron, J., Wang, Q., (2003), Striving for a Sustainable Mining Industry: Arsenic Control through an Integrated Approach. SGS Lakefield Research Limited, Mining and the Environment Conference Sudbury, Canada.

Heimlich, E., (2015), South & Central American Greenfield projects are key to future copper supply. CRU Insight, January Edition.

Mayhew, K., Bruce, R., Heidel, A., Kadereit, H., Mean, R. and Wagner, O., (2011), Unlocking Value in Copper Arsenic Sulphide Resources with the Cu-As CESL Technology, Hydrocopper Conference Proceedings, Viña del Mar, Chile.

Salomon-de-Friedberg, H., Robinson, T., Lossin, A., Omaynikova, V., (2014), Developing Copper Arsenic Deposits with CESL Technology, Conference of Metallurgists, Vancouver, Canada.

Sanchez, M., (2013), Chilean Mining Sustainability at a glance, Sustainability Rio de Janeiro, Brasil.

TMS 2005 – Arsenic Metallurgy Symposium, San Francisco, United States.

TMS-AIME 1988 – Arsenic Metallurgy Fundamentals and Applications Symposium, Phoenix, U.S.A.