DEVELOPING COPPER ARSENIC RESOURCES WITH CESL TECHNOLOGY

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ABSTRACT

In 2009, Aurubis AG and Teck Resources Limited, recognizing a growing industry need, joined together to advance and further develop technology to deal with arsenic-bearing copper concentrates in an effective and environmentally sustainable manner. The work that followed included extensive bench test-work and 3 months of continuous, fully integrated pilot campaigns on high arsenic-bearing copper concentrate as well as environmental testing, market studies and economic assessments. The success of the CESL Process in processing arsenic-bearing copper concentrates, at levels of up to 4.6% arsenic, has been previously presented. The present paper discusses aspects of similar, equally successful trials on copper concentrates with grades of arsenic approaching 12%. Key parameters to the successful processing of these types of concentrates are discussed. In addition, data on subsequent continuous, pilot gold recovery from the leach residues and the longer term stability characteristics of these residues are also included.

KEYWORDS

Copper concentrate, arsenic, CESL, scorodite, residue stability

INTRODUCTION

Demand for copper worldwide has increased significantly due to an ever increasing global population as well as technological development and industrial growth. According to the industry consulting services group, Wood Mackenzie, global refined copper consumption is forecast to increase at an average compound rate of 3.1% from 2013 to 2024 (Wood Mackenzie 2014).

In order to satisfy this growing demand for copper, primary copper from mining operations will continue to be the major copper source despite extensive efforts in recycling and developing trends in reduced per capita consumption through sharing programs and technological advancements. It is likely that copper mining projects, previously delayed or precluded from development due to factors such as lower economic grade, complex mineralogy, or increased levels of deleterious elements, will need to be reassessed.

Arsenic has been a growing concern for miners, smelters and refiners. It reduces the marketability of the concentrates and exposes miners to penalties when exceeding a concentration of 0.2% (CRU 2014). Increased arsenic levels in concentrates encounter technical (arsenic-in-anode) and environmental limits (concentration in off-gas, slag). Moreover, smelter capacity for treating high-arsenic concentrates is decreasing due to the ban on the import to China of copper concentrates with arsenic contents higher than 0.5% in combination with recent, stricter environmental regulations for several smelters dedicated to treating higher arsenic bearing concentrates (CRU 2014).

With the growing restrictions and limitations of existing pyro-metallurgical pretreatment and treatment processes, sustainable copper production from high-arsenic bearing copper concentrates will require new technologies and processes.

CESL PROCESS AS THE PREFERRED HYDROMETALLURGICAL OPTION

Recognizing the long-term strategic benefit of a new sustainable mine to metal solution for the development of high arsenic bearing copper deposits, Teck and Aurubis formed a partnership in 2009. A detailed metallurgical pilot plant campaign was undertaken at the beginning of 2010 to validate CESL hydrometallurgical technology for high arsenic (up to 4.6% As) bearing copper-gold concentrates. The results of the campaign were presented in two papers (Mayhew 2011, Bruce 2011). Later in 2012 Teck and Aurubis continued with bench test-work and two pilot plant campaigns processing concentrate containing up to 11.8% arsenic.

The following paper will present the technical feasibility of processing refractory minerals, such as enargite, with CESL technology. Successful copper extraction is demonstrated in bench and pilot plant results. Mineralogical characterization, as well as short, and long term residue stability results confirm the technology's capability to fix the arsenic in a form considered to be the most stable for environmental disposal – Basic Ferric Arsenate Sulphate (BFAS), previously identified as "Type 2" scorodite (Bruce 2012). Lastly, the economic viability of the technology is demonstrated based on green- and brownfield project business cases.

CESL Copper-Arsenic Technology

The CESL Copper Process flowsheet, as demonstrated in the fully integrated pilot plant, comprises the following steps:

- A pressure oxidation leach (200 psig) where copper sulfide minerals are oxidized at medium temperature (~150°C). During this step copper is leached into solution and arsenic is precipitated as a stable residue in a single processing stage.
- A solid-liquid separation step involving a counter current decantation circuit that separates leach liquor from the residue and simultaneously washes that residue.
- Solvent extraction and electrowinning circuits to purify and recover copper from the leach solutions.

- An evaporator to maintain the water balance of the hydrometallurgical circuit. Recovered condensate is used to wash the leach residues free of soluble metals, reducing fresh water needs.
- A neutralization circuit to control excess sulphate generated in the leach by precipitating gypsum.
- A bleed circuit for impurities, including a small SX extraction cell to remove Cu before precipitating impurities that would otherwise buildup in the circulating solutions – zinc, for example.

Figure 1 below presents the arrangement of the various unit operation described.
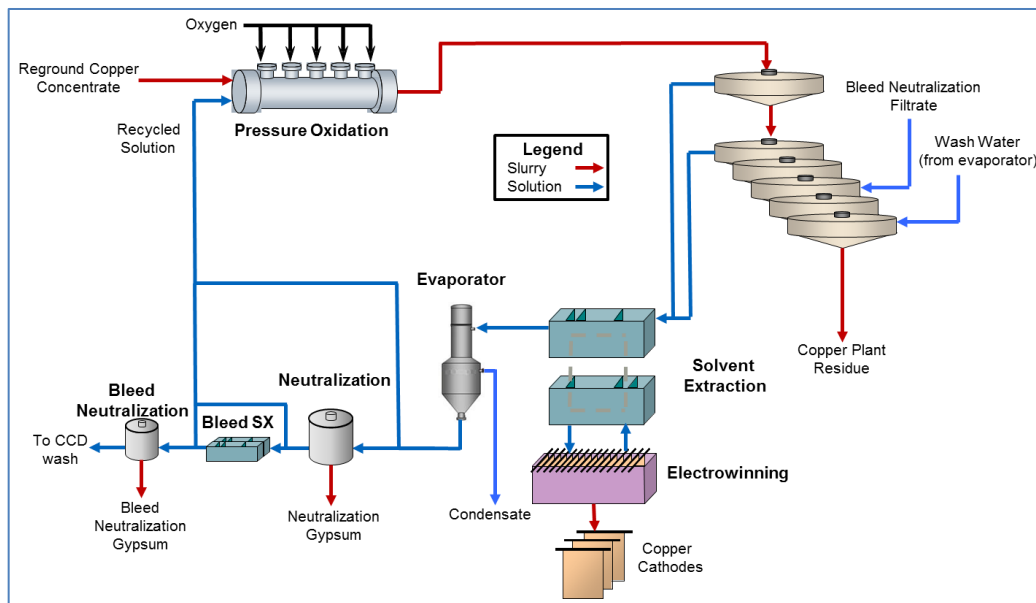

Figure 1 - CESL Copper Process flowsheet for treating Cu-As concentrates

Consequently, there are 4 solid products from the process: the copper cathodes, the autoclave leach residue, a gypsum residue, and a small impurity bleed residue. No liquid leaves the process other than what is entrained in the washed residues.

In many concentrates, the silver and gold values are appreciable and these report to the Copper Plant residue discharging from the CCD circuit. Recovering these precious metals involves a second circuit which is referred to as the CESL Gold Process shown in Figure 2.

The major steps for the recovery of gold and silver comprise:

- Adjusting slurry pH with lime and leaching the residues under oxygen pressure, at room temperature, in a cyanide solution for 60-90 minutes.
- Filtering and washing the now precious metal depleted leach residues prior to final impoundment.
- Recovering the precious metals in solution using a carbon-in-column circuit. Stripping the gold and silver from the carbon and recycling the carbon back to the columns. The precious metals are subsequently electrowon and converted into Dore metal.
- Cyanide and copper recovery by acidification, volatilization and reneutralization (AVR).
- Destroying residual cyanide in the bleed solution prior to final disposal.

The products of the flowsheet are gold/silver Dore metal, copper solids returned to the Cu Plant autoclave, iron-arsenic residues, and a solution bleed from the circuit.
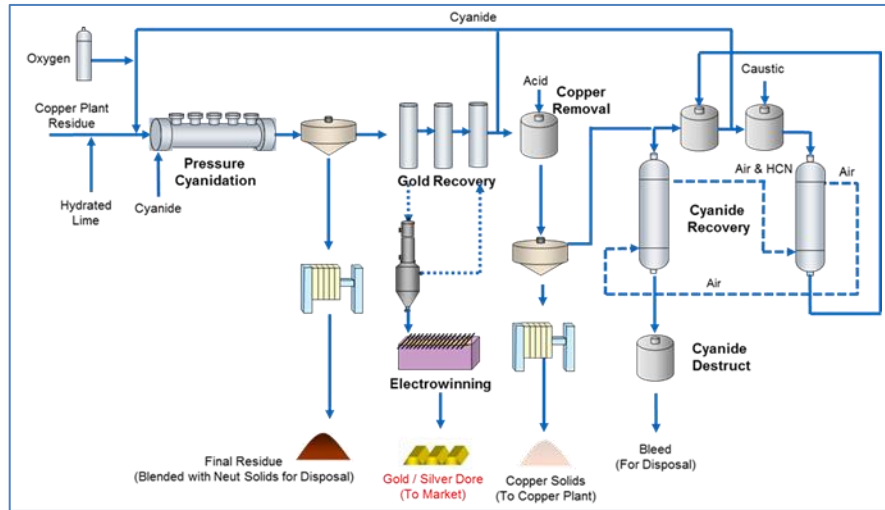
Figure 2 - CESL Gold Process flowsheet

Technical program

The purpose of the present program, carried out through extensive bench test-work and 3 separate pilot plant campaigns, was to assess CESL technology on sulphide feeds containing exceptionally high levels of arsenic. The compositions of the feed materials processed are shown in Table 1.

Table 1 - Copper concentrates tested

Concentrate	Cu %	As %	Fe %	Au g/t	Ag g/t
A	33.5	11.8	11.8	4.0	127
B	31.1	9.7	12.5	4.9	141
C	27.6	8.5	15.8	4.4	128
D	24.1	7.3	19.0	4.0	115

Arsenic concentrations ranged from 7 to 12% while copper levels were more typical, ranging from 24 to 34%. Iron concentrations were below those found in more typical copper concentrates. Other elements present in the concentrates at appreciable levels (>1,000 ppm) included Pb, Sb, Al and Ca, but these did not appear to play a significant role in concentrate behaviour during subsequent pressure oxidation. An estimate of the mineralogical breakdown of the concentrates is presented in Table 2 below.

Table 2 - Major mineralogical components of the processed concentrates

Mineral	Idealized Formula	Concentrate			
		A	B	C	D
Enargite and Tennantite	Cu_3AsS_4 and $Cu_{12}As_4S_{13}$	65	51	44	37
Chalcopyrite	$CuFeS_2$	8	8	6	4
Sphalerite	ZnS	-	3	3	3
Pyrite	FeS_2	21	23	34	44
Gangue		6	15	14	12

The key minerals in these studies proved to be enargite and pyrite; the enargite because of its refractoriness to leaching along with its arsenic content and the pyrite due to its acid generating tendencies. Enargite itself has little iron in its lattice so some of the pyrite acts as a valued iron source for the precipitation of stable scorodite type compounds in the leaching step.

RESULTS AND DISCUSSION

Cu Extraction & As Deportment

Demonstrating high copper extraction was a key deliverable in this test-work. Historical bench experiments had failed to exceed 80% copper extraction on concentrates having a similar level of enargite when using standard CESL conditions (Mayhew et. al.). Different factors influencing the copper extraction were extensively tested in small batch tests on a concentrate assaying 11.8% As to establish optimal conditions for pilot testing. These included grind size, retention time, residue recycle to autoclave, surfactant type and quantity, other additives, the concentrate composition itself (pyrite level, As:Fe ratio) and iron and acid levels in acid feed.

Bench test results

The example in Table 3 demonstrates the benefit of fine grinding when leaching enargite bearing material.

Table 3 - Impact of grind size on enargite leaching efficiency, concentrate A

Grind Size, p80 – µm	23	17	15	11	9	7
Cu Extraction, %	64.2	82.6	80.2	85.7	89.7	92.9

Feed solution: 12 g/L Cl, 8 g/L free acid, 15 g/L Cu, 5 kg/t surfactant

This series of tests showed that additional grinding prior to leaching, in conjunction with CESL conditions, could attack greater than 90% of the enargite mineral to improve copper extraction, however, neither surfactant type nor dosage nor retention time had been optimized at this stage.

In a different test series the impact of retention time was investigated.

Table 4 - Retention time series, concentrate A

Retention time, min	Cu Extraction, %	As Deportment to Residue, %
60	81.1	87
90	88.4	96
120	91.0	99
180	94.8	99

Feed solution: 12 g/L Cl, 10 g/L free acid, 14 g/L Cu, p80 = 22 um, 3 kg/t surfactant

Long retention times benefit copper sulfide conversion, as well as arsenic deportment to the residue. The optimal retention time was 90 minutes. The fineness of grind was not optimized in these trials.

The recycle ratio, the ratio of recycled residue to fresh concentrate that is sent to the autoclave, was varied as shown in Table 5. In this case, results were close to being optimal with fine grinding, the use of the preferred surfactant at the desired concentration and the 90 minute retention time.

Table 5 - Residue recycle to the autoclave, concentrate C

Recycle Ratio	Cu tot in Residue, %	Cu Extraction, %	As in Filtrate, mg/L
1.5	1.2	98.6	473
1.0	1.3	98.4	426
0.5	1.4	98.3	570
0	2.0	97.5	1510

Feed solution:12 g/L Cl, 40 g/L free acid, 12 g/L Cu, p80 = 7 um, 90 min RT

Recycling the residue from the autoclave back to the autoclave feed improved copper extraction and arsenic precipitation. Recycle ratios higher than 1:1 do not appear to significantly improve copper extraction nor promote additional arsenic precipitation.

Surfactant type and dosage also affect copper extraction. From the surfactants tested, 3 kg/t OPD appears to deliver the better result of 98.3% copper sulfide conversion versus 94.9% for aniline at the same dosage (Concentrate D, 90min RT, 7um p80; feed solution: 12 g/L Cl, 40 g/L free acid, 12 g/L Cu). Surfactant dosage series showed that higher surfactant dosage of a given surfactant was not necessarily beneficial for the copper extraction and this parameter needs to be determined for each concentrate as it is a matter of economic evaluation of the incremental conversion gained.

As indicated in Table 6, the addition of potassium iodide (KI) is beneficial to copper extraction. However, additions higher than 1 kg/t concentrate are difficult to justify economically.

Table 6 - Effect of KI addition on Cu extraction, concentrate D

KI Dosage, kg/t conc	0	0.25	0.5	1	6.5	13
Cu Extraction, %	96.2	97.8	97.6	98.4	99.3	98.4

Feed solution: 12 g/L Cl, 40 g/L free acid, 12 g/L Cu, P80 = 7 um, 90 min RT

Although the high copper extraction achieved was clearly an important milestone, arsenic deportment to autoclave leach residue was also viewed as an important characteristic of the process. From Table 4 and Table 5, it becomes apparent that longer retention times benefit arsenic precipitation, as does residue recycle to the autoclave. Recycling, not only effectively increases solids retention time, but also provides the opportunity for scorodite seeding to promote the desired form of arsenic precipitation.

Bench test-work showed, quite unexpectedly, that greater amounts of iron in feed relative to arsenic (a lower As:Fe ratio – Figure 3) do not necessarily favor greater arsenic precipitation.
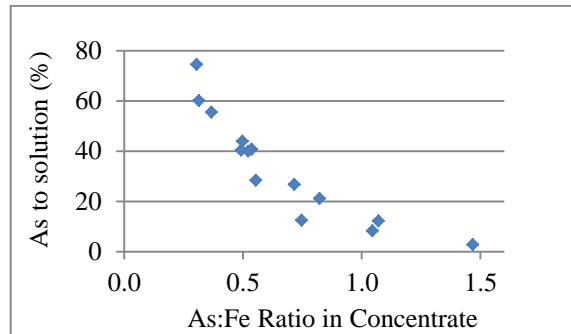

Figure 3 - Impact of the As:Fe ratio on the fraction of arsenic in solution for various concentrates

Table 7 provides average extraction results for the three different feed materials during piloting.

Table 7 - Average pilot plant metallurgical results

Concentrate	B	C	D	D with recycle
As in Feed, %	9.7	8.5	7.3	7.3
Pyrite in concentrate, %	23	34	44	44
As:Fe ratio	0.78	0.54	0.38	0.38
Cu Extraction, %	96.5	97.8	98.0	97.3

Copper extraction during leaching varied from 96.5 to 97.8%. The difference in extraction between "D" and "D with recycle" can be explained by the 2 um coarser grind in the latter case. Oxidation of the sulphide copper in concentrate in the autoclave was 98.5%+, but some copper is incorporated into the precipitating residue resulting in a lower overall extraction in the autoclave.

The essential element in achieving high copper extraction is the correct combination of fine grinding, halide addition, and surfactant. Residue recycle also improved copper extraction in the autoclave (Table 5). Higher copper extraction coincided with elevated levels of pyrite in the feed. The higher pyrite levels appeared to modestly impede copper co-precipitation into the iron residue.

The greatest extent of arsenic precipitation occurred near a molar ratio of As to Fe of 1 (a weight ratio of 1.34) in the feed material. When operating below this ratio, adding extra Fe in the form of pyrite or as iron sulphate counter-intuitively reduced the extent of arsenic precipitation. This result was mitigated to an appreciable extent in the pilot plant with residue recycling as demonstrated in Figure 4. Greater than a 1:1 residue to concentrate ratio was not found to be beneficial.
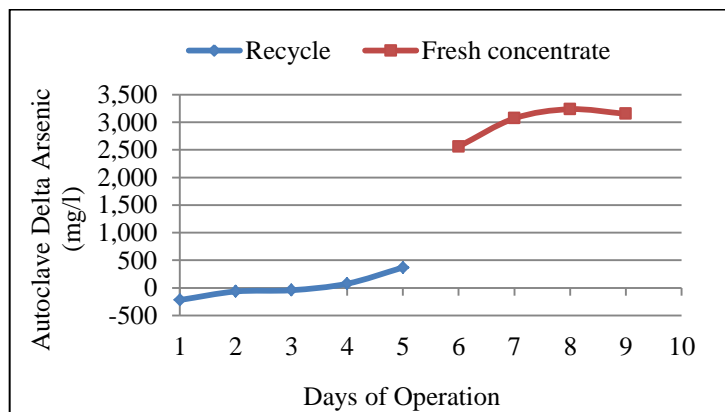

Figure 4 - Increasing As in solution as recycle is discontinued, concentrate D

Longer leach times also favor greater arsenic precipitation in the autoclave. For this reason, the "typical" leach retention time in the CESL Process was extended from 60 to 90 minutes. Any benefit to added copper extraction was slight.

Acid would be expected to impact the extent of arsenic precipitated in the autoclave, but this is a variable that is constrained by overall circuit considerations. For example, bench tests indicated that a feed acid level of 40 g/L minimized arsenic to solution, but combined with the extent of sulphur oxidation occurring in the autoclave, the final discharge solution acidity caused inefficiencies in the downstream SX operation so acid in feed to the autoclave was limited to 20 g/L. This outcome led to the realization that

excessive acid generating pyrite in feed was deleterious to the process in more than additional reagent costs and throughput limitations.

The results from these campaigns confirmed stable operation with high copper extraction from these high arsenic-bearing feeds and demonstrated the conditions for maximizing arsenic precipitation in the autoclave.

Precious metals extraction

The extraction of gold in the CESL Process is dependent on the mineralogy of the concentrate. Mineralogical analysis of the concentrate "B" indicated that approximately 60% of the gold was present as cyanide soluble native gold and electrum, while the remaining 40% was in the form of refractory telluride minerals. The mineralogy corresponds well to the average gold extraction achieved through piloting of 64%, with a similar silver extraction achieved. Of the unleached gold present in the Gold Plant "B" residue, 84% was found to be in the form of gold telluride minerals. With minimal gold telluride leaching, the overall 64% gold extraction corresponds to 90%+ leaching of the cyanide soluble native gold and electrum. This finding is consistent with test-work performed in 2011 at a fully integrated demonstration scale of the CESL Gold Process processing 1.5 t/d of feed material. More than 99% of the gold in the feed was in the form of native gold or as electrum and achieved greater than 90% gold extraction. High gold extraction is achievable when gold telluride minerals are not abundant.

Residue recycle to the autoclave, KI addition and pyrite grade of the feed material noticeably affected precious metals extraction in the Gold Plant. The addition of 0.5-1 kg/t KI leads to an increase in both Au and Ag extraction. Residue recycle of 1:1 fresh concentrate to recycled material modestly improves Au but negatively impacts Ag extraction. The adverse impact of residue recycle is partially neutralized with the addition of KI. Pyrite grade appears to correlate with precious metals extraction. Higher pyrite levels in the feed material saw lower precious metals extractions which might be influenced by the characteristics of the iron precipitated under the modified leach conditions.

Residue Stability

Short-term stability (TCLP)

Residues submitted for stability analysis had the following average compositions.

Table 8 - Compositions of residues submitted for TCLP evaluation

Residue	RT, min	As, %	Fe, %	As:Fe, wt.	S as SO4, %
B	90	13.8	17.7	0.78	1.9
C	90	9.1	15.8	0.58	2.8
D	90	9.6	16.7	0.57	3.4
D with recycle	90	10.4	16.6	0.63	3.4

The EPA Toxicity Characterization Leaching Procedure (TCLP) was used to assess short-term stability during the pilot plant campaign. This test conducts a leach of the residue over 18 hours at specified conditions. The resulting filtrate is analyzed for its metals content. Results are presented in Table 9.

Table 9 - TCLP results

Residue	RT, min	As, ppm	Cu, ppm	S, ppm	Zn, ppm
B	90	1.2	11	240	2.3
B	120	0.7	5	440	1.8
C	90	0.7	15	560	-
D	90	0.5	12	600	4.6
D with recycle	90	0.2	19	180	5.3
Environmental Limits		5[1]	100[2]	n/a	500[2]

[1]EPA Toxicity Characteristic 2014
[2]British Columbia Leachate Quality Standard (Environment Management Act 2009)

In all cases, TCLP results were well below the recognized EPA limit of 5 ppm for arsenic. The TCLP indicated that test outcomes improved with higher pyrite levels in the concentrate. The longer retention times improved the result of the test although not nearly as effectively as the recycle of residue through the autoclave. Soluble sulphur releases during the TCLP test appeared to increase with higher levels of pyrite. For the residue recycle test, a significantly lower amount of sulphur was noted in the leachate.

Arsenic dissolution from residues ranged from only 0.004% to 0.017%.

By the EPA's definition, all these residues would be considered non-hazardous material with regards to arsenic as well as the other monitored constituents, which represents one of the key positive attributes of the process.

Long-term stability data

Though the short term TCLP response is important, the longer term behaviour of residues when stored for protracted periods of time is critical. 2 L test bottles containing residue at a 20:1 liquid to solid ratio were monitored while being subjected to mild agitation at room temperature. The equipment used was an orbital shaker (Lab-Line Instruments Orbit Shaker, No. 3590) at 100-110 rpm and 2 cm lateral motion.

The long-term trials are ongoing with the copper residue from the pressure oxidation step. There was minimal change in solution arsenic concentration over the nearly 700 days of testing conducted so far with filtrate averaging 0.2 mg/L As.

The impact of varying pyrite in concentrate, blending the residues with limestone, and blending residues with mine tailings on arsenic dissolution trends was assessed. Characteristics of the leach residue following cyanide leaching to recover precious metal values combined with neutralization residues are also being investigated.

All tests seem to follow a common pattern where there was initial arsenic in solution on Day 1 followed by an ongoing reduction over time as the soluble arsenic steadily adsorbed over time. Data are presented graphically as the initial peak observed in Day 1, the test average for the entire period, and the value at Day 550. Higher pyrite (D vs C) appeared to slightly favor lower long-term arsenic values as shown in Figure 5.

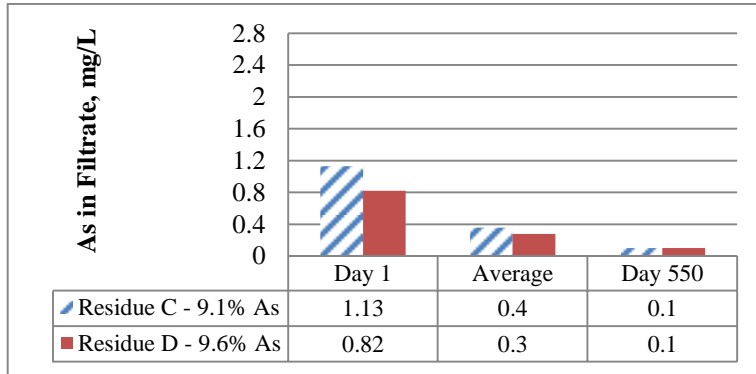|	Day 1	Average	Day 550
Residue C - 9.1% As	1.13	0.4	0.1
Residue D - 9.6% As	0.82	0.3	0.1

Figure 5 - Impact of pyrite in concentrate on apparent As stability in residue

After a period of time, it would not appear that there is any difference in the two residue types. Blending the leach residues with mine tailings may also be an opportunity. Figure 6 compares the results of leach residue alone with the residue diluted 1:1 with mine tailings and diluted 1:10 with mine tailings.

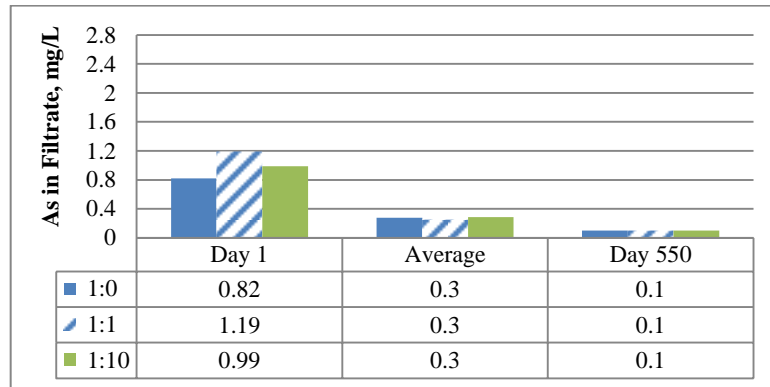|	Day 1	Average	Day 550
1:0	0.82	0.3	0.1
1:1	1.19	0.3	0.1
1:10	0.99	0.3	0.1

Figure 6 - Blending leach residue with varying amounts of mine tailings

The results show differences on Day 1, but thereafter mine tailings additions play little role in influencing soluble arsenic levels in filtrate. This test-work demonstrates that co-disposal of the residue with tailings may be a technically viable option, and site specific management scenarios need to be assessed to determine if separate leach residue disposal or co-disposal is favoured.

Adding varying amounts of limestone to the leach residue was not found to be a recommended strategy for stability improvement, as illustrated in Figure 7.

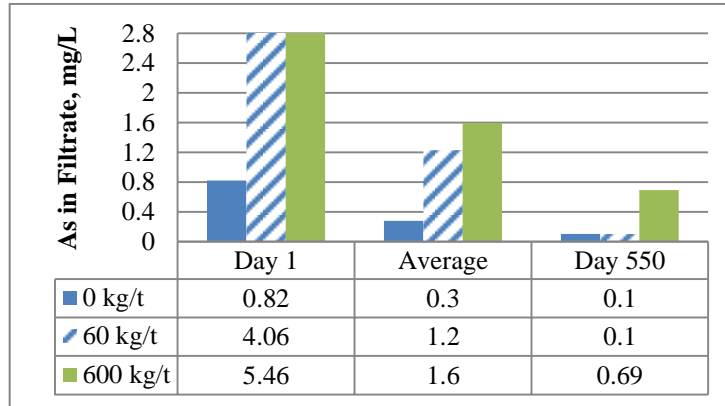|	Day 1	Average	Day 550
■ 0 kg/t	0.82	0.3	0.1
◢ 60 kg/t	4.06	1.2	0.1
■ 600 kg/t	5.46	1.6	0.69

Figure 7 - As leaching with 0, 60 & 600 kg/t of limestone added to residue

The greater the amount of limestone added, the more arsenic was found in filtrate, regardless of the sample timing. However, in all cases, there was a reduction in arsenic levels in filtrate with time and As in filtrate never exceeded EPA guidelines.

Both TCLP and longer term stability work indicate that the residue produced is stable. A further positive feature of this type of residue is that its arsenic shows limited biological accessibility (Mayhew et.al. 2011).

CASE STUDY

A conceptual case study was prepared which demonstrates the economic feasibility of developing a copper-arsenic deposit by means of the CESL technology. The integration of a CESL leaching plant into an existing SX-EW facility at a depleted heap leach site is also evaluated (Brownfield case).

The case study includes mine, mill and CESL refinery costs associated with developing a 20 year project which would produce 200,000 t/a copper cathode, 64,700 oz/a gold, and 1,295,000 oz/a silver. The concentrate feeding the CESL refinery was assumed to contain 27% copper and 1.5% arsenic.

The mine and mill capital cost were estimated at US$20,000 per annual tonne copper for Greenfield and US$15,000 per annual tonne copper for Brownfield sites. Capital cost estimates for the CESL refinery used factored equipment costs whose sizing was based on process heat and mass balances which utilized extensive data collected from numerous previous pilot and demonstration plant campaigns. Similar sized equipment costs quoted in feasibility level studies were used wherever possible. All equipment costs in the benchmarking studies were estimated by independent third-party engineering consulting firms and all factoring was completed by Teck. The data set of quoted equipment costs were converted to 2014 costs using a GDP inflation factor.

The indirect refinery costs included EPCM, temporary construction facilities, camp and catering, third party engineering and field services, major spares, first fills, freight, operating manuals and training. A contingency of 30% was used on the refinery total direct and indirect costs. The project capital costs are summarized in Table 10.

Table 10 - Case study capital cost summary

Capital Cost Estimates		Greenfield Project	Brownfield Project
Mine Mill Capital*	US$/tpa Cu	$20,000	$15,000
Refinery Cost Element			
Directs	US$M	$487	$310
Indirects	US$M	$426	$290
Refinery Total		$940	$600**

*Wood Mackenzie 2014
**Includes an allowance for integration into an existing SX/EW Plant

The mine and mill operating costs were estimated at US$ 1.20/lb Cu based on Wood Mackenzie (SNL 2013). The refinery operating costs were calculated at US$ 0.36/lb of copper (reagents and consumables, labour, power, and maintenance cost). Typically, reagents comprise 20-25% of the operating cost. Limestone and oxygen account for the largest portion. Any sulphur that is oxidized completely to sulfate consumes oxygen and generates acid that must be subsequently neutralized at significant cost. The limited sulfur oxidation to sulfate across the autoclave is one of the benefits of the CESL Cu-As technology when compared to total oxidative leach (TOL).

Financial Results

The main assumptions underlying the economic analysis are a long-term copper price of US$ 3.50/lb, a long-term silver price of US$ 11/oz, and a long-term gold price of US$ 1,214/oz. Post-tax net present values (NPV) are discounted at 8%. Mine, mill and refinery performance factors of 50% and 85% were assumed for Year 1 and Year 2 of the operations respectively. Mine and mill sustaining capital was estimated at 1% of the capital cost and the refinery sustaining capital was estimated at 2% of the capital cost.

Table 11 presents the valuation results for the case study.

Table 11 - Case study economic valuation results

Financial Summary	Greenfield	Brownfield
Average Free Cash Flow (FCF)	$877M	$891M
NPV (8%)	$2440M	$3650M
IRR	14%	20%

Developing an arsenic containing copper-gold deposit can be economically feasible with today's long term metal price assumptions. With a break-even copper price of US$ 2.00/lb Cu for Greenfield and Brownfield options (pre-tax), the economics associated with a project of this scale are attractive. Brownfield SX/EW sites offer a clear advantage due to their reduced capital requirements.

CONCLUSIONS

The processing of high arsenic bearing copper concentrates at levels of up to 10% arsenic was successfully demonstrated in continuous, fully integrated pilot campaigns processing roughly 40 kg/d of concentrate.

Copper extractions in excess of 96.5% were achieved from concentrates containing chiefly enargite. Arsenic was effectively captured in an iron residue during the same copper leaching step. Gold was readily recovered from the leach residue except for the portion that was tied up as a telluride. Silver recovery from residue was variable and improved when the concentrate pyrite grade was lower.

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 1.5 years have shown no tendency for arsenic leaching from residues containing up to 15% arsenic. These tests continue.

A case study examining a mine-mill-CESL refinery option for producing 200 kt/yr of copper cathode indicated favorable economics, particularly if the location were a heap leach operation with available SX/EW capacity, that was nearing the end of its useful life.

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