

UNLOCKING VALUE IN COPPER ARSENIC SULPHIDE RESOURCES WITH THE COPPER–ARSENIC CESL TECHNOLOGY

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ABSTRACT

The copper market shows evidence of supply constraints going forward and as such the development of metallurgically challenging deposits will be required to meet the increasing demand. Recognizing the potential value in arsenic-challenged copper deposits, Aurubis and Teck have worked jointly to develop the technology necessary to process these difficult concentrates economically and responsibly. The CESL Process offers an attractive method for processing arsenic-bearing copper concentrates. CESL performed bench and pilot scale testing on four different arsenic challenged concentrates in 2010 with arsenic grades ranging from 0.7% to 4.6%. The main minerals of interest for this work were enargite and tennantite. Pilot plant testing demonstrated high extraction of copper (97%) from such concentrates with near quantitative deportment of arsenic to the residue. A detailed study is underway that assesses the medium-term stability of the residue.

INTRODUCTION

Demand for minerals continues to grow with expansion in global population and wealth, requiring the development of non-traditional resources in order to meet future mine supply [1]. Non-traditional resources are expected to be more complex, with lower grade ores containing increased levels of impurities such as arsenic [2]. Several Greenfield copper projects in South America and the Pacific Rim are challenged by high levels of arsenic including El Galeno, Canariaco Norte, Caspiche, Tampakan, and Frieda River [3, 4].

Gradual depletion of high grade ore with low levels of arsenic is a growing concern within the copper industry [5]. Penalties incurred by miners for arsenic in concentrates have increased significantly because the removal and disposal of arsenic is difficult and costly for smelters [6] and because the environmental challenges are increasing worldwide. During the smelting process arsenic forms as hazardous arsenic oxide dusts and fumes that are challenging to manage in the smelter environment are not easily stabilized for safe disposal [7]. Typically miners incur penalties on arsenic in concentrates above 0.2% As with smelter rejection limits of 0.5% [8]. This essentially precludes the development of several large copper resources via conventional smelting.

Among the options for arsenic control in the metallurgical treatment of copper concentrates is the precipitation of scorodite, which is widely accepted as the most suitable method for stabilizing arsenic [9]. The pressure hydrometallurgical approach to processing high arsenic bearing copper concentrates is a favorable option as mineral extraction and arsenic fixation can take place in a single autoclave vessel. Under CESL pressure leaching conditions (150°C, 1380kPa) high copper extraction and arsenic fixation as scorodite is possible.

Arsenic control in the copper industry ultimately needs an integrated approach involving each stage of the value chain, i.e. exploration, mine operation, refining process and mine closure. Teck Resources Limited (Teck), Canada's largest diversified mining company and Aurubis, Europe's largest copper producer, have formed a partnership to work together on advancing the application of CESL copper-gold technology for the development of high arsenic bearing copper resources.

This paper will present the metallurgical findings from recent pilot plant testing on high-arsenic concentrate samples.

BACKGROUND

Teck has developed hydrometallurgical processes collectively known as the CESL Processes. The CESL Processes are cost competitive, thoroughly tested and capable of processing a wide range of materials including copper, copper-gold, and copper-nickel concentrates. The CESL Processes as applied to copper has been successfully assessed on a semi-industrial scale [10].

Recent bench testwork has established that optimized CESL conditions can effectively treat concentrates that contain elevated arsenic, including those that contain appreciable amounts of the refractory mineral enargite [11]. These results yielded a copper extraction of 97% with moderate sulphur oxidation. The majority of the arsenic (~99%) was precipitated in the pressure oxidation autoclave. XRD analysis indicated the presence of >20% S° and >50% scorodite in the bench residue with no additional crystalline ferric arsenate phases being identified [11].

In order to verify the application of the technology to high arsenic bearing Cu and Cu-Au resources, a pilot study was performed to demonstrate high metal recoveries from such concentrates (0.7% to 4.6% As). The pilot program was designed to verify the bench results, further define the flowsheet, provide residues suitable for subsequent gold recovery testwork, and collect necessary data for the design of such plants.

As Aurubis and Teck are committed to responsible mining and refining practices, a primary focus of the pilot operations was to characterize the chemical behavior of residues over time, including assessing environmental and extrinsic factors that affect residue stability. In addition, there was a focus on arsenic health and safety, with an emphasis on data collection to effectively address future questions from external stakeholders.

OBJECTIVES

The main objectives of the pilot plant campaign were as follows:

1. **Achieve high copper extraction and recovery.** CESL has achieved high copper extraction from enargite bearing concentrates on the lab scale [11] and the aim in the pilot plant was to validate these results on a continuous basis. Pilot plant operations were fully integrated and thus provided an assessment of overall copper recovery which has a significant impact on the plant economics.
2. **Produce LME Grade A cathode.** The CESL Process has historically produced a cathode product that consistently meets LME Grade A standards for chemical composition [12]. This is achieved through the application of industry standard solvent extraction technology and demonstrating this feature of the process is a standard element of all CESL campaigns.
3. **Quantify the deportment of arsenic to the plant residue.** The deportment of arsenic to the CESL plant residue in the concentrate leach stage is a key benefit of the Cu-As CESL technology. This is desirable as any arsenic that does not report to ferric arsenate in the autoclave can potentially be lost to tailings as a soluble loss or less stable precipitate. High soluble arsenic tenors are also undesirable from an industrial hygiene perspective.
4. **Produce residue for environmental stability testwork.** Demonstrating the production of a stable arsenic-bearing residue was a key objective of the pilot campaign through mineralogical and stability testing. The residue from the integrated plant is currently undergoing a rigorous stability test program.

CAMPAIGN DETAILS

CESL Copper Process description

The CESL Copper Process flowsheet consists of five main process steps:

1. **Pressure oxidation:** copper mineral is oxidized and leached
2. **Counter current decantation:** residue solids are washed
3. **Solvent extraction:** production of high purity copper electrolyte
4. **Electrowinning:** recovery of copper in a commercial product form
5. **Neutralization:** removal of excess acid (sulphate) to a gypsum residue

A graphical representation of the Cu-As CESL technology flowsheet is shown in Figure 1.

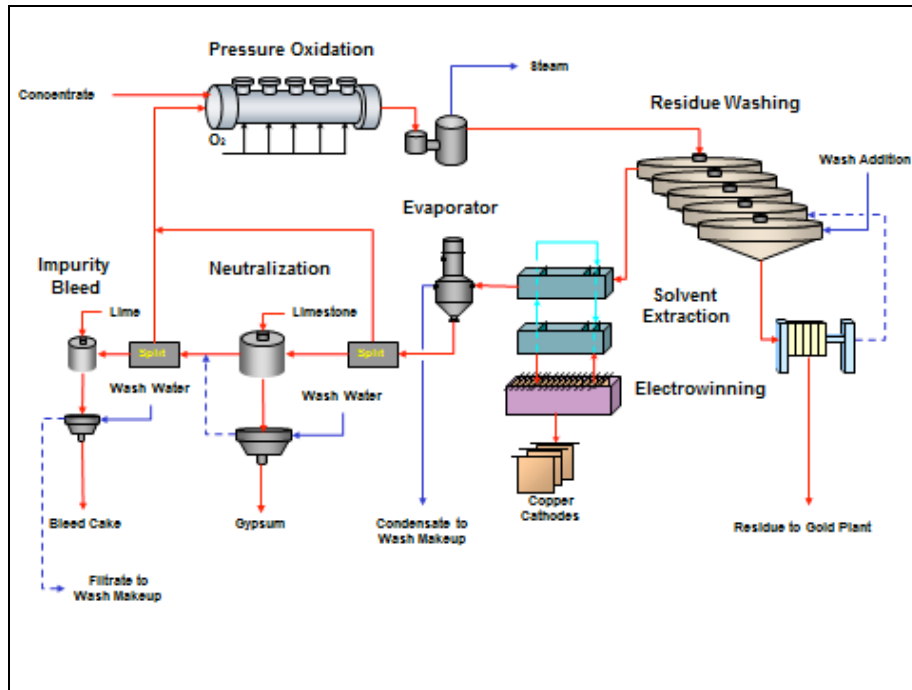
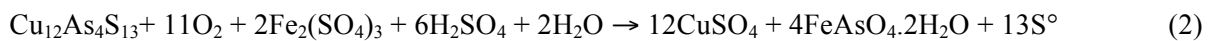
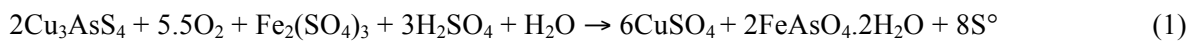


Figure 1: Cu-As CESL technology flowsheet

Details of the CESL Process have been well documented in previous publications, and only elements specific to copper arsenic sulphides are briefly discussed below [12].

Pressure oxidation involves oxidation of sulphide minerals at elevated pressure and temperature in the presence of catalytic chloride ions. In the case of arsenic bearing concentrates, a significant portion of the copper value can be found in minerals such as enargite (Cu_3AsS_4) and tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$). The overall oxidation chemistry of these minerals reacting in the autoclave is presented below:



Within the autoclave the copper is solubilized and the arsenic reacts with iron to precipitate as ferric arsenate. Previous CESL testing and literature suggests that CESL autoclave conditions (150°C, 1380kPa) favors the formation of a scorodite product ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) [13,14,15]. The iron for this reaction is supplied through the dissolution of hematite in the autoclave.

In addition to the unit operations required for the oxidation, leaching, and recovery of copper, an evaporator is used to control the plant water balance and two neutralization circuits are used to control the sulphate and minor metals content in the plant inventory. Further details on these process steps can be found in previous publications [12].

Feed composition

During the copper arsenic pilot plant campaign (hereafter referred to as the Cu-As Campaign) four separate concentrates were processed. Each of these concentrates contained levels of arsenic in excess of the Chinese smelter import limit of 0.5% [8]. The major elemental compositions for the concentrates processed are presented in Table 1.

Table 1: Elemental composition of concentrates processed

Element	Unit	A	B	C	D
Cu	%	21.2	25.8	27.1	29.5
Fe	%	24.5	24.5	24.9	19.6
S	%	26.8	36	33.9	33.5
As	%	0.7	1.4	1.5	4.6

The concentrates for this testwork were selected to allow for the arsenic concentration to be progressively increased. This gradual increase in arsenic grade (from 0.7% to 4.6%) allowed for the collection of air quality monitoring samples to ensure that occupational exposure to arsenic and other metals was maintained at a level well below the WorkSafe British Columbia exposure limits. It was of metallurgical interest to test a range of arsenic grades that reflected concentrates with arsenic content (1%-1.5% As) as well as a concentrate with elevated levels of arsenic (>4% As). The copper, iron, and sulphur content of the material processed varied over ranges typical for copper sulphide concentrates.

The mineralogy of the concentrates processed is given in Table 2.

Table 2: Concentrate mineralogy

Mineral (%)	Formula	A	B	C	D
Chalcopyrite	CuFeS_2	43	22	49	38
Bornite	Cu_5FeS_4	8	6	10	7
Luzonite/Enargite	Cu_3AsS_4	--	5	6	20
Tennantite	$\text{Cu}_{12}\text{As}_4\text{S}_{13}$	--	1	2	2
Chalcocite	Cu_2S	1	13	--	--
Covellite	CuS	2	5	4	5
Pyrite	FeS_2	9	38	20	18
Pyrrhotite	FeS	10	--	--	--
Arsenopyrite	FeAsS	2	--	--	--
Gangue	-	23	9	9	8

The minerals of particular interest for this work were enargite, luzonite, and tennantite. These minerals typically display a refractory character that poses a challenge for hydrometallurgical processing [17]. The variation in pyrite grade within the various concentrates allowed for the assessment of any impact on metallurgical performance and to assess if this parameter played a role in long-term residue stability.

Campaign scope

The extensive Cu-As campaign processed 4.8 tonnes of concentrate material, operating on a 24 hour/day, 5 day/week schedule. Availability and production data is presented in Table 3, with the pilot facility (capacity 35 kg/day cathode) achieving availability greater than 90%.

Table 3: Campaign production, consumption, and availability

Measure	Unit	Value
Availability	%	91
Hours Runtime	h	1934
Concentrate Processed	kg	4803
Cathode Produced	kg	1050
Gypsum Produced	kg	2293
Bleed Cake Produced	kg	348

The copper pilot plant operates a fully integrated flowsheet and includes all product streams and inventory management measures that would be incorporated in a full scale Cu-As CESL refinery.

RESULTS AND DISCUSSION

Metallurgy

Some past attempts at hydrometallurgical processing of concentrates containing copper arsenic sulphide minerals have been hampered by low copper extractions or difficulties in dealing with the arsenic solubilized during the leaching process. This section aims to demonstrate that the Cu-As CESL technology can effectively extract copper from these refractory minerals while precipitating arsenic in a single stage.

Copper Extraction and Recovery

Previously published bench scale testing has shown copper extractions of up to 97% can be achieved from high-enargite concentrates using the CESL Process [11]. Achieving similar copper extraction results on a continuous basis were one of the key objectives of the pilot plant campaign. The copper extraction achieved for each of the four concentrates processed is presented in Table 4, with extractions ranging from 97-98%.

Table 4: Copper extraction results

Feed Material	Copper in Concentrate (%)	Copper in Residue (%)	Copper Extraction (%)
Concentrate A	21	0.8	97
Concentrate B	26	1.0	98
Concentrate C	27	1.2	97
Concentrate D	30	1.3	97

Generally a retention time of 60 minutes is sufficient for the copper sulphide minerals to oxidize and leach in the CESL Process. While processing concentrates containing copper arsenic sulphide minerals,

however, a longer retention time of 90 minutes was required. An extraction profile from the continuous pilot autoclave is shown in Figure 2.

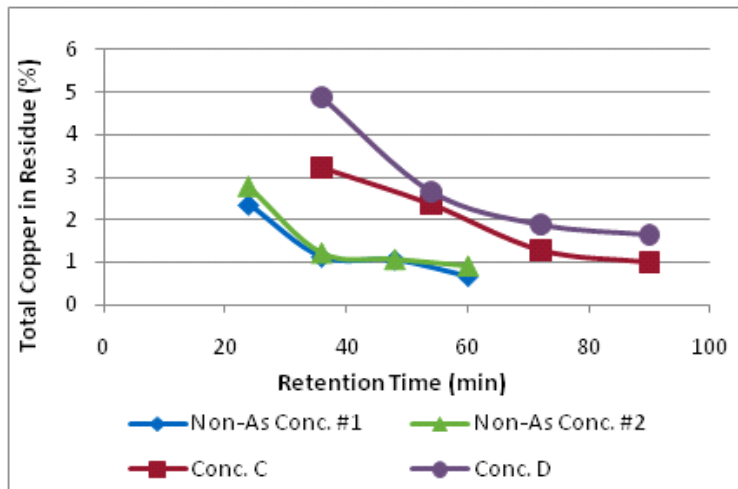


Figure 2: Copper in residue of autoclave compartment samples

Copper extraction from two non-arsenic concentrates processed during a previous campaign is largely complete after 40 minutes with the balance of the retention time giving a small increase in extraction. For the arsenic-bearing concentrates the reaction can be seen to proceed more slowly with significant decreases in copper content being achieved through to 70 minutes. This can be related to the copper contained in enargite and tennantite being more difficult to oxidize and extract than the copper hosted in chalcopyrite, bornite and other copper sulphide minerals [17,18]. Figure 3 presents the residue composition as determined by mineral liberation analysis for concentrate C. This data shows that the unreacted sulphide minerals remaining in the residue (labeled as “Other”) are composed primarily of unreacted pyrite with copper arsenic sulphides being present in relatively the same abundance as other copper sulphide minerals.

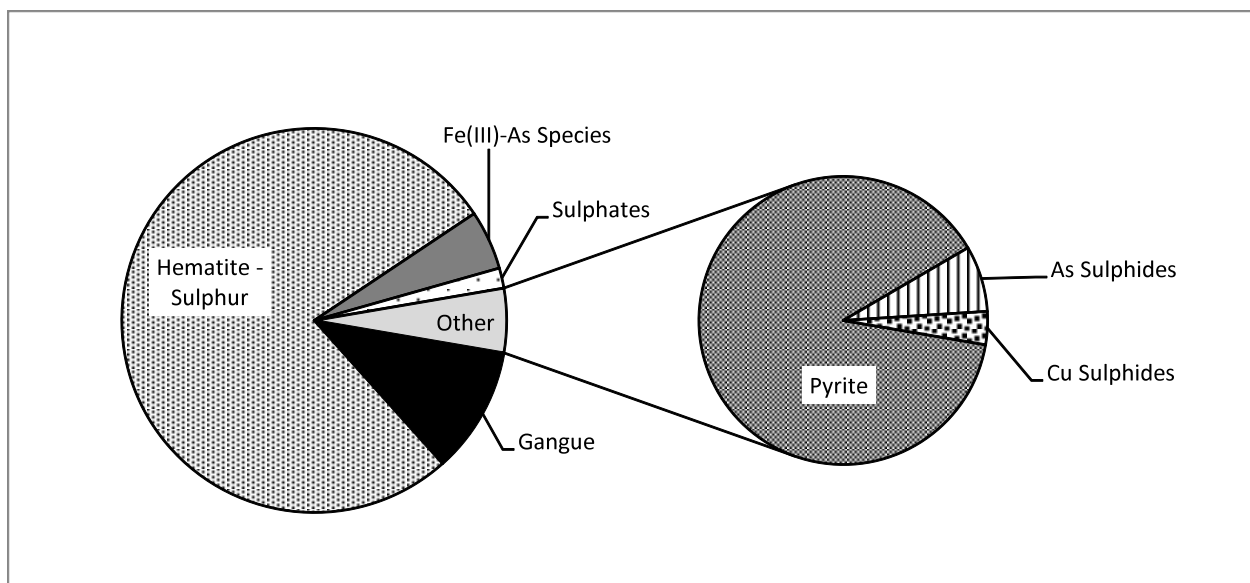


Figure 3: Residue composition for concentrate C

Though copper extraction is an important measure of success in the processing of copper concentrates, the degree to which this copper is recovered to cathode is equally important. The department of copper to streams leaving the copper plant is presented as a Sankey diagram in Figure 4.

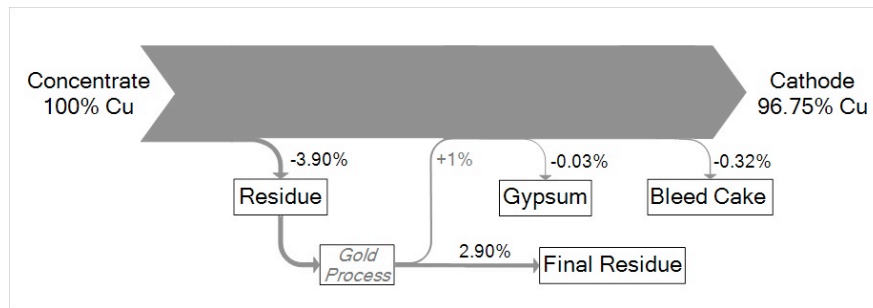


Figure 4: Copper Sankey diagram

The copper recovery exceeded 95% during copper pilot plant operations. Application of the CESL gold process has shown that a small amount of copper contained in the copper plant residue leaches in the gold plant and can be recycled to the copper plant for recovery. This increases the copper recovery for the plant to greater than 96%. Further optimization of this recovery is believed to be feasible, specifically in regard to residue and bleed cake losses.

A final measure of the performance of the copper plant is the quality of the copper cathode produced. Table 5 presents the average chemical assays for the cathodes sampled and LME Grade A standards. Of the cathodes sampled only one did not meet LME Grade A standards due to an elevated level of lead which was attributed to inclusion of lead from the anodes into the cathode matrix resulting from weekend shutdown.

Table 5: Cathode quality

g/t	Pb	Bi	As	Sb	Sn	Fe	Ni	Ag	S	Se	Te
LME Grade A	5	2	5	4	5	10	10	25	15	2	2
Cathode Average	2.7	<0.1	<0.5	<1	<0.5	<1	0.3	<1	6.5	0.2	<0.1

Arsenic Department

The department of arsenic is quantified as it must be shown that its management is well understood and controlled. The preferred form for disposal of arsenic is as a scorodite product ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and literature has shown that precipitation in an autoclave at 150°C favours scorodite formation above other, less stable arsenic containing materials[13,14,15,16]. The department of arsenic for each concentrate processed is presented in Table 6. Iron is also presented as it is required for arsenic precipitation as scorodite.

Table 6: Deportment of arsenic and iron

Output stream	Conc. A		Conc. B		Conc. C		Conc. D	
	Fe	As	Fe	As	Fe	As	Fe	As
Deportment to Residue	99.3%	99.9%	98.0%	99.6%	95.3%	98.7%	98.0%	99.7%
Deportment to Gypsum	0.1%	0.0%	0.4%	0.1%	1.0%	0.3%	0.4%	0.1%
Deportment to Bleed Cake	0.6%	0.1%	1.7%	0.3%	3.7%	1.0%	1.6%	0.2%
Autoclave Discharge Solution (mg/L)	868	3	7900	90	5100	65	3500	170

Previous studies have shown that a certain molar ratio of iron to arsenic is required in order to ensure that the precipitation of scorodite can proceed as required. Under atmospheric conditions this ratio has been listed as 4:1/Fe:As in order to ensure that scorodite is formed [16]. Other studies that have precipitated scorodite in an autoclave at elevated temperatures (150°C – 175°C) have shown that a lower molar ratio of iron to arsenic would still allow for the formation of scorodite [15]. During each portion of the campaign the iron tenor was sufficient for precipitation of arsenic as scorodite.

Sulphur Oxidation

Limited sulphur oxidation to sulphate across the autoclave is one of the benefits of the Cu-As CESL technology when compared to total oxidative leaching (TOL). Any sulphur that is oxidized completely to sulphate consumes more oxygen and produces sulphuric acid that must be subsequently neutralized at a cost. The sulphur oxidation for each of the concentrates processed is shown in Table 7. This value is calculated using two methods; a sulphate balance around the autoclave and by oxygen consumption. The sulphate balance method assigns any gain in sulphate to the oxidation of sulphur, while the oxygen consumption method discounts the amount of oxygen required for the oxidation of metals and assigns any remaining oxygen consumption to the oxidation of sulphur.

Table 7: Fraction of sulphur in concentrate feed that was oxidized

Sulphur Oxidation	Conc. A	Conc. B	Conc. C	Conc. D
Sulphate Balance	27%	47%	42%	44%
Oxygen Consumption	25%	49%	39%	43%

These values for sulphur oxidation are higher than those typically seen in the CESL Process, which usually range from 5-25%. This is attributed to the elevated levels of pyrite in the concentrates processed as well as the extended autoclave retention time of 90 minutes. These values are still below half of the sulphur oxidation that would result from TOL technology (complete oxidation of sulphur present).

Minor Elements

In addition to arsenic, several smelter penalty elements were contained within the concentrates. These elements included antimony, bismuth, mercury, and tellurium. The processing of these constituents showed near quantitative deportment to the residue stream, with no concentration increase detected across the concentrate leach.

Health and Safety

The Environmental, Health and Safety (EH&S) program at CESL strives to ensure that all employees return home safe and healthy every day. In order to ensure that occupational exposure to arsenic was at a low level two types of monitoring were conducted: air quality monitoring and monitoring of inorganic arsenic in the urine of selected workers. The air quality results during the campaign were all below the

limit set by WorkSafe BC for exposure to arsenic during a 12-h shift of 0.005 mg/m³. All biological monitoring samples were also well below the action limit of 50 µg As/g creatinine during the Cu-As campaign. These samples were taken at the beginning and end of an operators shift rotation to identify whether an increase in arsenic levels had occurred.

Environment

As the arsenic deportment to the CESL plant residue was near quantitative (refer to Table 6) determining the environmental stability of the residues was seen as an important step towards permitting of a potential project. The EPA Toxicity Characterization Leaching Procedure (TCLP) was used for this analysis during the pilot plant campaign. This test conducts a leach of the residue over 18 hours at specified conditions and analyses the resulting filtrate for metals content. Of the 64 residue samples submitted for TCLP analysis during the pilot plant campaign, 34 resulted in an arsenic concentration in filtrate below the detection limit of 0.1 mg/L. Of the remaining 30 samples the average concentration of arsenic detected was 0.15 mg/L with a standard deviation of 0.06 mg/L. All values fell well below the failure limit for landfills in British Columbia of 2.5 mg/L arsenic in filtrate.

Further Work

The TCLP testwork discussed above was used as a preliminary indication of the environmental stability of the arsenic bearing residue produced in the Cu-As CESL technology. As all residues tested passed for arsenic, a more rigorous residue stability program is required. An external consultant with expertise in arsenic stability and characterization of arsenic bearing residues was contacted and provided aid in developing a residue stability program.

The first steps of this residue stability program are currently underway and include:

1. A full characterization of the residues produced by XRD, MLA and FTIR methods.
2. A multi-stage diagnostic leach of the residues produced to differentiate between water soluble, weak acid dissociable and strong acid dissociable compounds.
3. Mild agitation, 8-week leaches conducted under various conditions (temperature 25°C and 40°C; potential 50mV, 300mV, and oxic; pH 5 – 9, controlled and drifting) at an external environmental lab.

The completion of this work will allow for a greater understanding of the species present in the residues, their behaviour under various conditions, and the long-term storage option that should be pursued in future projects. This will also lead to standard humidity cell testing under the proposed long term storage conditions.

As the majority of arsenic-rich Cu concentrates contain appreciable gold and silver values, effective recovery of these metals is an intrinsic part of any hydrometallurgical processing technology. As gold and silver deport to the copper plant residues a program has been initiated to evaluate gold and silver recovery using the CESL Gold Process.

CONCLUSIONS

Together Teck and Aurubis successfully advanced the application of the Cu-As CESL technology for future development of high arsenic bearing copper resources. The following conclusions were drawn from the collaborative pilot testwork completed in 2010:

1. High copper extraction (97%) was achieved from concentrates containing significant amounts of copper arsenic sulphide minerals (20%).
2. High copper recovery (>96%) was attained while operating a fully integrated copper pilot plant.

3. Copper cathode produced met LME Grade A standards on a consistent basis.

Further work should serve to confirm long term stability of arsenic as well as the economic recovery of precious metals from the copper plant residues. Based on well-established academic findings with respect to arsenic stability from medium temperature pressure leaching and historical precious metal leaching results from the CESL Gold Process, these items are not expected to pose significant future challenges. This clearly positions the Cu-As CESL technology as a lead processing alternative for arsenic bearing copper concentrates, opening the door for the successful development of large copper orebodies that have been precluded from development due to the current arsenic constraints known to traditional smelting technology.

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