The use of Albion Process™ to produce Copper Sulfate reagent for use in Zinc flotation (Case Study) *

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Abstract

Glencore Technology's Albion Process™ is a combination of ultrafine grinding and oxidative leaching at atmospheric pressure, providing a proven effective, safe, and robust approach for oxidizing sulfidic materials. This paper describes an innovative application of the Albion Process™ in an existing zinc flotation operation, who had approached Glencore Technology to design and commission an Oxidative Copper Leach plant to produce a suitable Copper Sulfate reagent from refinery produced Copper Cementation Cake (Copper Mud). The site had previously operated a copper sulfate crystal reagent mixing and dosing system, however it was found that the purchasing and transportation of copper sulfate crystal resulted in unacceptably high operating costs. The Albion Process™ plant supplied by Glencore Technology successfully produced the required reagent on site at a fraction of the cost and provides flexibility in both potential feed sources and production rate to suit site requirements.

1. Introduction

Copper sulfate is an integral part of zinc flotation. Copper sulfate is added as an activator to enhance the performance of xanthate collectors through the substitution of a CuS site, which in turn reacts with xanthate to increase hydrophobicity (Wills & Finch, 2015; Frederick Ravitz & Wall, 1934; Dichmann & Finch, 2000; Wang, Liu, & Zeng, 2013). For many remote mine sites, the cost of transporting critical reagents, such as copper sulfate crystal, can constitute an avoidably high proportion of operating costs. Thus, sites may seek alternative means of producing their own copper sulfate. While some sites have adopted the process of leaching copper oxide to make copper sulfate, the financial benefits of this approach are not ideal as the process still attracts a high cost in materials and transportation.

Another alternative may be the use of refinery produced copper cementation cake (i.e. copper mud), a high-grade copper waste stream from zinc refining, as an alternate and inexpensive feed source to produce copper sulfate. Copper cake is a readily available by-product of the zinc refining process however contains a range of impurities including cadmium, lead, iron, and arsenic. The high impurity of these penalty metals has historically precluded the copper cake from being used for industrial copper sulfate manufacture. As copper mud is priced in the same manner as copper concentrate, it is far less costly than higher purity products obtained through reagent suppliers. A previous study has suggested that up to 70% of copper from high copper zinc plant residue could be leached into solution (Sethurajan et al., 2019), however the leaching process is typically mass diffusion limited, and requires an oxidant to maximize reaction kinetics and process efficiency (Li, Wang, Wei, Wang, & Barati, 2018; Li, Zhang, Min, & Shen, 2013; Sethurajan, et al., 2016).

Glencore Technology was commissioned by an existing Zinc concentrator with historically high reagent costs due to its remote location. The largest proportion of ongoing expenditure was attributed to copper sulfate, contributing to nearly 30% of operational expenses (more than $25 million per annum). It was identified that introducing a reagent plant to produce copper sulfate on site could lead to significantly reduced operating costs, as well as offering other environmental and operational benefits. This paper describes the testwork and subsequent novel application of Glencore Technology's Albion Process™ to address barriers to leaching copper mud for the generation of copper sulfate for an existing Zinc operation.

2. The Albion Process™

The Albion Process was developed in 1994 by Glencore and is a globally patented technology comprised of two stages. In the first stage feed material undergoes ultrafine grinding in an IsaMill™ to generate greater surface area and minimize potential passivation of the leaching mineral surface. The second step involves oxidative leaching in the Albion Oxidative leach Reactor™ during which oxygen is injected at supersonic velocities via Glencore Technology's patented HyperSparge™. The HyperSparge™ offers efficient oxygen mass transfer into solution ensuring the process is not oxygen mass diffusion limited (Voigt, Mallah and Hourn, 2017).

The process occurs auto-thermally at atmospheric pressure; base metals are targeted using acidic conditions, whilst concentrates containing precious metals such as gold and silver undergo leaching in mildly acidic conditions (approximately pH 5.5). Target base metals are solubilized, after which they are recovered from solution via downstream processing such as SX/EW or precipitation. In the case of precious metals, these remain within the solid residue which is then subjected to cyanidation or equivalent gold extraction process.

The Albion Process™ has been commercialized in zinc and gold with five plants in operation and reported on extensively (Hourn & Turner, 2010; Hourn & Turner, 2012; Voigt, Hourn, & Mallah, 2016; Senshenko, Aksenoz, Vasiliev, & Seredkin, 2016). With proven applications in base metals and gold, it is a low cost, safe, and effective hydrometallurgical solution to the ever-complicated metallurgy landscape. Due to its simple layout and atmospheric conditions, it avoids the myriad of safety and process issues that may be associated with other oxidative leaching approaches. The Albion Process™ also boasts operating costs up to one third lower compared to other oxidative leaching processes (McNeice, Marzoughi, Kim, & Ghahreman, 2021; Aylmore, 2012).

3. Methods

Testing was undertaken in three phases. Phases one and two consisted of bench scale testwork undertaken at Murdoch University and Brisbane Met Labs (BML) respectively, whilst Phase three was comprised of site trials.

3.1 Phase 1: Sample characterization and preliminary leach testwork (Murdoch University)

Murdoch University were commissioned to characterize four potential sources of copper cake and initial viability of leaching in terms of valuable metal extractions, the potential evolution of hazardous toxic gases including arsine (AsH_3) and stibine (SbH_3) during the leaching, and the mineralogy of the subsequent leach residue.

Four copper cake samples were considered and analysed by Murdoch University:

- Sample 1: Copper Mud (Germany)
- Sample 2: Copper Mud (Canada)
- Sample 3: High Copper Cement (Spain)
- Sample 4: Low Copper Cement (Spain)

Head and residue characterisation comprised elemental analysis (Thermo Scientific ICP-MS instrument, model iCAP-Q ICP-MS) and mineralogical analysis (XRD using a GBC Enhanced Multimaterial Analyser (EMMA)).

Preliminary leach test work

Batch leach tests were performed at 5% and 30% solids, 80°C and four hours leach duration, followed by hot water dilution before cooling and settling overnight (~16 hours total test duration). Tests commenced via the addition of solids and water to the reactor, then adding the condenser and scrub solution (distilled water containing 1% peroxide at pH 10) before the required sulfuric acid was added. The tests targeted variations in the percentage of new sample added to the leach feed (25, 50, 75 and 100% of new sample in the leach feed) where approximately equal portions of the remaining feed source samples were added to provide similar total copper grades in the combined feed.

3.2 Phase 2: Bench scale leach testwork (BML)

BML were commissioned to optimize leach conditions by investigating:

- Copper extraction from successive leaching of selected copper mud sample.
- Effect of varying the stoichiometric acid ratios on the leaching process.
- Optimal air dispersion methods to reduce leach time.

Tests were carried out on a composite sample, generated from ten separate bags containing Sample 2 copper mud (identified as the preferred source of copper mud during Phase 1). Composite grades are summarized in Table 1.

Table 1: Phase 2 Copper Mud Leaching Testwork Composite Sample Grades

Sample	Cu (%)	Zn (%)	Pb (%)	As (ppm)	Cd (ppm)
Composite	66.7	3.6	3.2	96	38,474
Maximum Grade	68.7	5.5	4.7	218	40,853

Testwork was performed in a 3L baffled beaker using an overhead stirrer. Approximately 170g of wet sample (108g dry) was added to the vessel and water added to make a 7.46 %w/w slurry. The air was sparged at 5L/min and H2SO4 additions made based on a stoichiometric ratio of 115%. The pH and ORP were monitored, and the reaction was complete when the ORP had increased and stabilized for 1 ½ hrs.

3.3 Phase 3: Plant trials

‘Scaled up’ site-based trials were conducted across four campaigns in November and December 2016, to confirm the results of bench scale testwork. Existing plant infrastructure was utilized, including a specially lined, fully enclosed 280 cubic meter tank with high energy mixing, air sparging and a wet scrubber system. Copper cake and water were mixed in an existing sodium carbonate mixing tank, and then transferred to the 280m^3 tank. Acid was added to target a 115% stoichiometric ratio, and air sparged into the tank at a rate of 2500 – 3000m^3/h. After settling for 12 hours, the solution was transferred to Copper Sulfate holding cells. A solution sample was taken and submitted for assay and residue from the 280m^3 tank was pulped, sampled, and transferred to Thickener 3 (Figure 1).

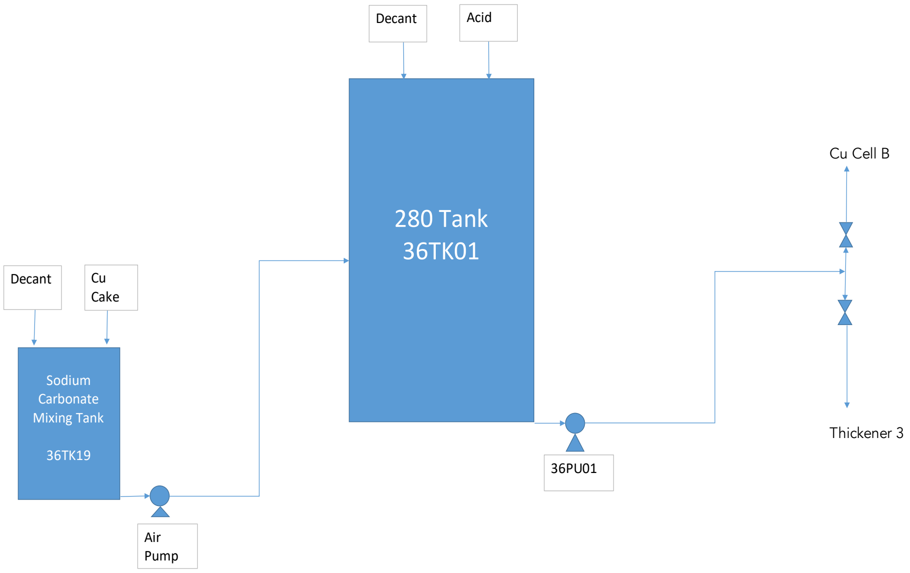

Figure 1: Copper Cake Leaching Site Trials Equipment and Circuit

4. Results

4.1 Phase 1: Sample characterization and preliminary leach testwork (Murdoch University)

The compositions of the four different copper mud feed options are summarised in Table 2.

Table 2: Copper Mud Leaching Sample Characterisation

Sample	Cu	Zn	Cd	Fe	Pb	As	Co	Ni	SG	P80
Sample 1 (Germany)	56.5	4.4	3.8	4.4	1.3	7.8	2.1	0.3	4.7	186.2
Sample 2 (Canada)	61.1	5.4	4.6	3.5	1.2	0.1	0.5	0.3	3.3	29.2
Sample 3 Low grade copper cement (Spain)	40.9	13.3	2.6	6.2	1.4	0.1	13.2	1.2	3.1	31.5
Sample 4 High grade copper cement (Spain)	86.0	2.2	0.3	2.7	0.5	0.1	1.1	0.2	5.3	16.9

XRD analyses show that the main copper phases present in the feed were Cu metal and Cu_2O. Sample 1 exhibited a significantly coarser 'as received' size distribution, higher arsenic grade, and lower copper grade compared to the other three.

Comparable copper extractions (~50%) were achieved across all preliminary leach tests performed by Murdoch University. These extractions were lower than expected, and residual Cu metal and Cu_2O in the leach residue suggested incomplete dissolution of the Cu into solution. Lower recoveries were most likely due to the absence of an oxidant (no oxygen sparging included during the leach tests).

The formation of arsenic gas was very low, with less than 1% of the contained arsenic in the feed reporting to the scrub solutions. Thermochemical modelling indicated that minimal arsenic volatilization could occur under the tested conditions. Due to the presence of iron most of the remaining arsenic is expected to form in scorodite ($FeAsO_4.2H_2O$), with any remaining iron precipitating out as goethite (FeOOH).

Sample 2 copper mud (Canada) was selected as the feed source for the reagent plant in consideration of its high copper grades, low arsenic content, finer grind size and comparable leach performance.

4.2 Phase 2: Bench Scale leach Tests

Successive leaching leaving sediment from preceding batching in the reactor achieved 100% copper extraction with each cycle, with no change to the final solution quality (Figure 2).

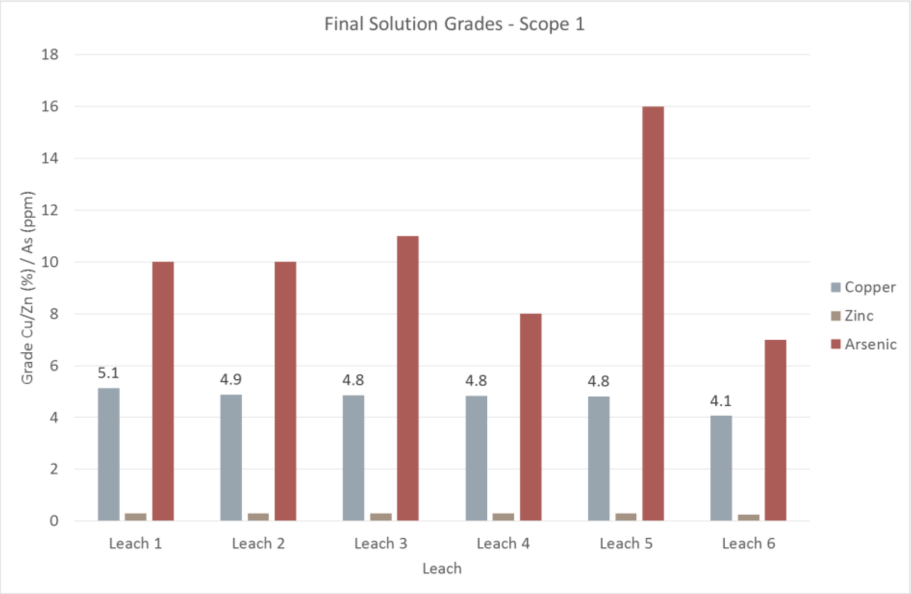

Figure 2: Final Solution Grades of Successive Leach Tests

Reducing the stoichiometric ratio of acid additions below 115% resulted in a decrease in the solubility of arsenic and an increase in liquor pH, however copper extractions were simultaneously compromised, declining to approximately 91% (Table 3). Thus 115% was selected as the optimal ratio for acid addition.

Table 3: Cu & As extraction, grades & pH across Stoichiometric Ratios for Acid Addition to Copper Mud Leach

Stoichiometric Ratio		**113%**	**108%**	**103%**	**98%**	**93%**	**89%**
Extraction to Solution from Solid Basis	Cu (%)	89	91	95	91	84	81
	As (%)	100	100	100	27	20	9
Solution Grade	Cu (%)	5.00	5.08	5.27	5.11	5.47	4.68
	As (ppm)	6.3	14.2	14.0	0.5	0.2	0.3
End Solution pH		1.22	1.37	3.07	4.17	4.01	4.31

4.3 Phase 3: Plant Trials

The copper extraction results achieved during the four plant campaigns are summarized in Table 4. Plant trials supported the findings of bench scale testwork. Leach performance overall was good, yielding an average copper extraction of 97.6% at a residence time of 6 hours.

Table 4: Copper Mud Leach Plant Trial Results

Campaign	**Date**	**Campaign Batches**	**Cu Recovery**	**Leach Time (Hours)**
1	15/11/2016	Batch 1 - 8	98.8%	5.7
2	23/11/2016	Batch 9 - 15	97.8%	7.6
3	02/12/2016	Batch 16 - 23	96.9%	6.5
4	08/12/2016	Batch 24 - 28	97.0%	4.6

5. Reagent Plant Engineering

The principal objective was to design a leaching plant capable of accurately and safely producing a 3.8 – 4 % w/w copper sulfate solution from Copper Cementation Cake. A block flow diagram for this process is below in Figure 3.

The plant was designed on a nominal feed rate of 760 kg/hr of wet copper cake, which is stored in a Mass Flow Hopper and metered into the Copper Slurry Tank. The Copper Slurry Tank agitates the copper cementation cake in water to form a slurry. The Copper Slurry Tank Agitator is designed for off-bottom mixing of slurry to a target density of 30% solids w/w.

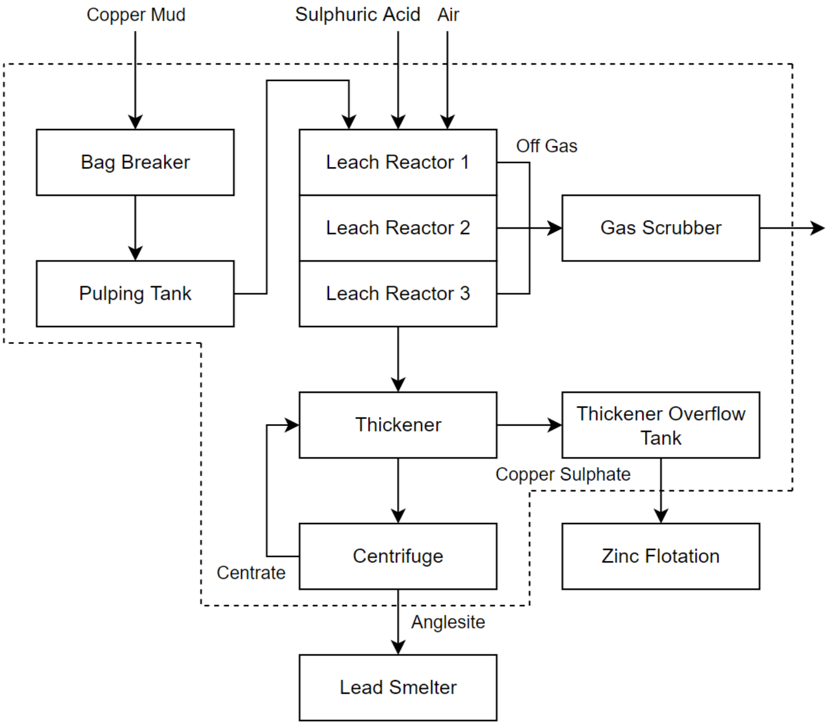

Figure 3: Reagent Plant Block Flow Diagram

The slurry is then pumped to the leach circuit, where leaching is performed in a series of three Oxidative Leach Reactors using dilute sulfuric acid and injected air. The design assumes a copper recovery of at least 97% and allows for a total residence time of 6 hours (2 hours per reactor), in line with the site trials. Each Leach Reactor will be fabricated from suitable material such as SAF 2507 (UNS S32750) alloy and agitated by a centrally mounted Leach Reactor Agitator, fitted with two, four bladed, wide blade axial flow impellers designed for high gassing rates. All agitator shafts and impellers will be fabricated from the same material as the reactors.

Acid and air will be added in a calculated excess to an assumed feed assay, consequently the variability of acid consuming species in the copper cake will affect the amount of air and acid available in the first reactor for the slower copper reactions. Dilute sulfuric acid at a nominal 200 gpl will be added to the Leach Reactors at 115% of Cu stoichiometry. The majority of the acid will be dosed to the first reactor and the remainder used to maintain target pH in the remaining reactors. Compressed leach air at 750kPag will be added to each Leach Reactor via up to four HyperSparge™ air spargers. The spargers will be designed to balance the sparger and agitator power input to provide the most efficient oxygen mass transfer.

The leach circuit will operate under atmospheric conditions, and reactors will be closed, with exhaust gas directed to a single vent feeding a central manifold that will direct off gas to the exhaust gas system. The leaching stage will operate auto-thermally. The leach reaction will be exothermic, and the heat of reaction will maintain slurry temperature at approximately 60°C. Raw water will also be added to the leach train to tightly control the copper tenor to 3.8% w/w or 42 gpl, required for optimal concentrator performance.

On completion of the leach, slurry gravitates to an Oxidative Leach Thickener, with the thickener underflow dewatered in a Centrifuge. The centrifuge cake will be manually consolidated with other lead sulfate materials for transport to a lead smelter. Centrate reports back to the Oxidative Leach Thickener and from there to the thickener overflow, which will be stored as reagent for the site Concentrator. A rendered image of the copper leach plant is provided in Figure 4.

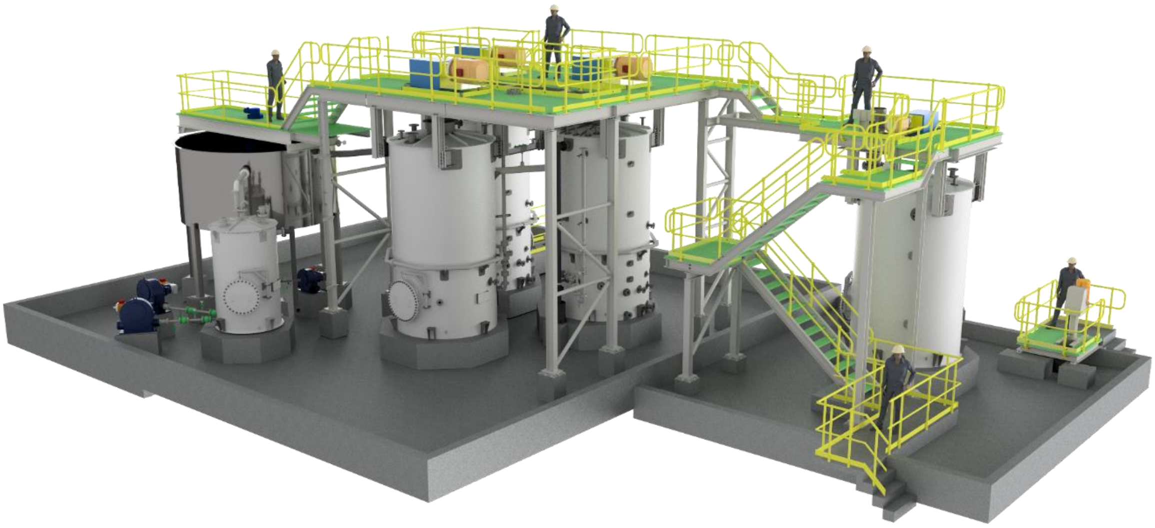

Figure 4: Base design with slurry feed

6. Reagent Plant Benefits

The copper leach plant will provide significant cost savings to the existing operation. The transportation of copper cake is more efficient compared to that of copper sulfate crystals. Copper cake typically presents with copper grades of 40-70 wt%, compared to approximately 25.5 wt% copper in the copper sulfate pentahydrate. This significantly reduces the volume of material and transportation required to produce the same amount of copper sulfate. At an average minimum grade of approximately 60% the copper cake equivalent material is less than half of the copper sulfate reagent, equating to a reduction in material handling and shipping of 600 tonnes each month. Copper mud is priced in the same manner as copper concentrate. As the range of impurities, including cadmium, lead, iron, and arsenic preclude copper from being used for industrial copper sulfate manufacture, it is substantially cheaper compared to its high purity counterparts. The reduction in required material for transport coupled with substantially lower costs contributes to the significant economic savings that copper cake leaching will provide the zinc operation.

The presence of penalty elements such as arsenic, cadmium, and lead in the copper mud effectively eliminates the use of copper mud in industrial copper sulfate manufacturing. As such Zinc refineries are required to either store or dispose of the copper mud that is generated during the purification stage. A reagent plant offers a solution to repurpose processing waste, thus ameliorating the cost of storage or disposal whilst simultaneously reducing operating costs associated with reagent consumption in the flotation circuit.

Finally, the residue of the reagent plant is mostly anglesite ($PbSO_4$), a by-product which may also be repurposed to create a new revenue stream. Due to its low solubility in sulfate systems anglesite precipitates immediately after being leached from the copper mud. It can then be easily recovered via filtration and transported to a lead smelter for incorporation into existing feed.

7. Conclusions

This paper offers insight into a new application for Glencore Technology's Albion Process™ technology, offering the Micro Albion™ Reagent Plant as a viable product for sites that wish to combat the large operating costs of copper sulfate, and potentially other reagents. Bench scale testwork indicated the extraction of high amount of copper (nearly 100%) from copper cake was technically feasible, supported by scaled plant trials. Based on the results of testwork and plant trials, a copper leach plant was designed and is due to be commissioned in Q3 2022. The copper leach plant will provide the zinc concentrator with a process critical reagent well within the required specifications and also provide a reduction in operating cost. This application opens the door to a smaller scale Albion leaching plant that can be applied to a wide range of materials containing a variety of valuable metals that are not being taken advantage of like refinery mud and electrostatic precipitation (ESP) dust. Producing process critical reagents on site at a fraction of the cost by leveraging more efficient and cost-effective materials shipping and handling, while reducing waste and emissions from transportation and repurposing process by products as additional streams of income.

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