UTILIZING CYANIDE RECOVERY TECHNIQUES IN THE CESL GOLD-SILVER PROCESS

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ABSTRACT

The CESL Gold-Silver Process was developed as an important value enhancing technology to recover gold and silver from residues produced from the CESL Copper Process (or other hydrometallurgical processes). To reduce the risk associated with full scale implementation of the CESL Gold-Silver process, a demonstration plant was operated continuously for 5 months in 2011 using a fully integrated flowsheet. An integral part of the flowsheet utilized acidification-volatilization-reneutralization (AVR) technology to recover and recycle cyanide. The CESL Gold-Silver Process cyanide recovery circuit uses a technique similar to Sulphidization, Acidification, Recycling and Thickening (SART) technology but does not require a reducing reagent for sulphidization because of the presence of thiocyanate in solution.

The AVR circuit operated with greater than 95% availability during the demonstration period of the campaign, including achieving 99% cyanide recovery efficiency within the stripper and absorber columns. A total of 150,000 liters of barren process solution was processed through the AVR circuit at a flowrate of 3.7 L/min and achieved an overall cyanide recovery of 93%.

This paper describes the cyanide recovery process used in the CESL Gold-Silver Process and the results from the demonstration plant campaign.

Keywords: gold, silver, cyanide, CESL, demonstration campaign, fully integrated

INTRODUCTION

A total of 100M ounces of gold was produced from mining in 2016 worldwide [U.S. Geological Survey, 2017], the majority of which was produced using cyanidation. Gold is, and has been, produced using a variety of methods including direct recovery of alluvial gold using gravity separation, amalgamation with mercury, or as a byproduct of base metal smelting where it is recovered in anode slimes during electrorefining. However, cyanide leaching continues to dominate as the primary production method for gold. Many alternative lixiviants have been studied and proposed but very few can compete with cyanide with respect to its strong selectivity, competitive cost, and ease of stripping and recycling. Very specific metallurgical properties have necessitated the use of alternatives at select sites such as at Barrick's Gold Strike mine where the unusual refractory nature of the ore has led Barrick to build the first ever commercial thiosulphate leaching plant. However, cyanide leaching remains the primary method for the recovery and production of gold worldwide, and likely will be for the foreseeable future. Silver is predominantly produced as a byproduct of base metal processing but is also produced using cyanide leaching.

Cyanide use is heavily regulated due to its profile as a highly toxic substance. However, cyanide can be transported and stored in solid form, typically as a sodium cyanide salt, and there exists a world trade market where it is produced at central locations and distributed for use elsewhere.

Sodium cyanide requires transportation to site and proper treatment after use for disposal. It currently ranges in price from \$2000 - \$3000 per tonne and has historically cost more than \$6000 per tonne. Recycling for reuse in the gold leaching circuit is critical to maintain the cost effectiveness of using cyanide. Fortunately this can be performed relatively easily.

Cyanide in solution is combined with gold ore and leaches the metal to form a soluble cyanide gold complex. The gold is then typically adsorbed onto activated carbon for downstream recovery. The resulting barren solution, still containing cyanide but absent of gold, can then be recycled for reuse and leaching of new ore. However, many gold bearing ores also contain copper. The presence of copper reduces the effectiveness of gold leaching as it also forms a cyanide complex thereby reducing available cyanide for gold leaching. This is particularly problematic for recycling of cyanide (in ores containing copper) because the copper concentration continues to grow with each pass of the solution, eventually inhibiting gold leaching. SART technology was developed specifically to break apart the copper cyanide complex thereby removing the copper from the gold leach solution and allow effective recycle of cyanide back to the leaching circuit. The first step in the SART process is sulphidization where sulphur ions are added to the solution stream. This ensures that during the second step, when the pH is lowered, the copper precipitates as chalcocite (Cu_2S) and not as copper cyanide (CuCN). Producing chalcocite is advantageous over copper cyanide for three reasons: 1) it reduces cyanide losses to the precipitate; 2) it improves the marketability and handling of the copper byproduct; and 3) it decreases the solubility product of the copper precipitate, helping with complete removal of the copper. The last steps in the SART process are recycling of cyanide and thickening of the copper precipitate.

The CESL Gold-Silver Process was developed as an important value enhancing technology to recover gold and silver from residues produced from the CESL Copper Process (or other hydrometallurgical processes). Residues from the CESL Copper Process contain small amounts of cyanide soluble copper as well as elemental sulphur. Upon contact with cyanide a portion of the elemental sulphur leaches to form thiocyanate (SCN^-) which ultimately increases the cyanide consumption of the leach. The CESL Gold-Silver Process uses pressure cyanidation to reduce gold and silver leaching time from conventional lengths of 24-48 hours down to 60-90 minutes to minimize thiocyanate leaching. Gold and silver are recovered from the resulting leach solution using conventional Adsorption Desorption Regeneration (ADR) technology using activated carbon. A portion of the resulting barren solution is treated using Acidification Volatilization Reneutralization (AVR) to recover and recycle cyanide to the front end of the leach and produce a copper byproduct and the remainder is directly recycled back to the cyanide leach. Despite the quick leach time, the formation of some thiocyanate is inevitable. While the cyanide that forms thiocyanate represents a loss of cyanide, the anion plays an important role in the cyanide recovery circuit. Upon pH reduction in the CESL Gold-Silver Process AVR circuit, thiocyanate in solution precipitates with the copper to form copper thiocyanate (CuSCN). The presence of the thiocyanate ensures that sulphur ion additions are unnecessary, unlike in the SART process, and copper cyanide precipitation does not occur, like it does in traditional AVR circuits.

To reduce risk associated with full-scale implementation of the CESL Gold-Silver Process, a demonstration plant was operated for 5 months in 2011. The demonstration plant operated 24

hours a day, 7 days a week processing 1.5 tonnes per day on a fully integrated basis with all recycle streams incorporated. A simplified flowsheet for the demonstration plant is displayed in Figure 1.
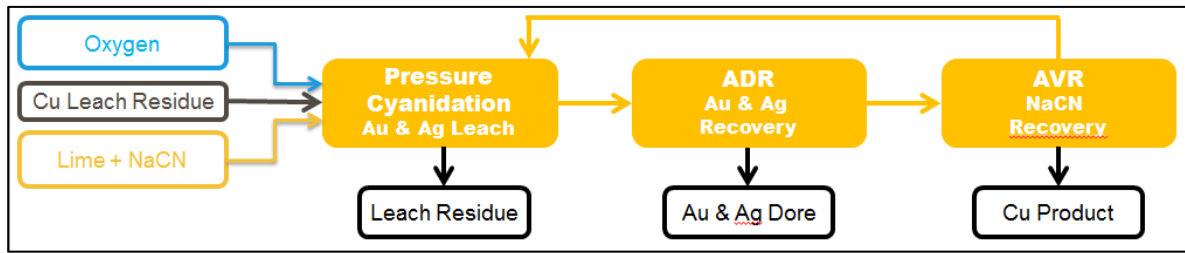

Figure 1 - Simplified CESL Gold-Silver Process Flowsheet

An integral part of the flowsheet is the AVR circuit used to recover and recycle cyanide. The circuit offers an elegant solution for recovering cyanide while producing a value-add copper byproduct, particularly when paired with the CESL Copper Process where the material is treated to recover the precipitated copper. Operation of the circuit provides high efficiency of recovery of cyanide fed to the circuit which benefits overall cyanide consumption as well as reduces costs associated with treatment of the bleed stream. Furthermore, the circuit produces a very low cyanide concentration effluent that can be easily treated and sent to a tailings pond to manage the water balance of the process.

AVR technology, or a variation of, is used commercially at multiple operations globally including Cerro Vanguardia in Argentina, Golden Cross in New Zealand, Akbakai in Kazakhstan, DeLamar in Idaho, and Morro de Ouro in Brazil [M. Botz, 2004, Unifield Engineering, 2006]. The objectives of operating the AVR circuit integrated with the rest of the CESL Gold-Silver Process at a demonstration scale were to reduce risk associated with equipment scale up including design, operability, and health and safety. Additional details of the AVR circuit design and performance for the demonstration plant are provided in the following sections.

PLANT DESCRIPTION

Location

The CESL Gold-Silver Process demonstration plant is located at Teck Resources Limited's facility in Richmond British Columbia, Canada.

Scope

The plant is designed to operate 24/7 with a throughput design capacity of 1.5 – 4 dry metric tonnes per day depending on desired pressure cyanidation vessel retention time. The precious metals recovery circuit is designed to produce up to an ounce of precious metals per day. A more detailed version of the flowsheet, as operated in the demonstration plant, is shown in Figure 2.
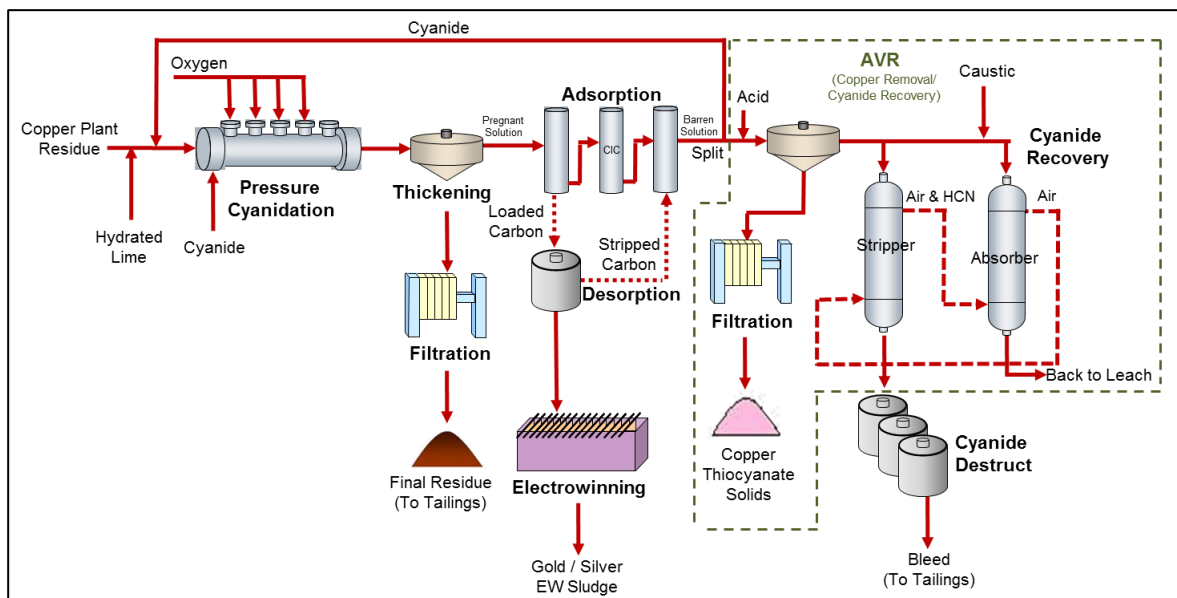
Figure 2 - CESL Gold-Silver Process Demonstration Plant Detailed Flowsheet

The demonstration plant operated with all flowsheet components fully integrated including process solution and solid recycle streams. The final product was a gold and silver electrowinning sludge with a precious metals content of 80% gold and silver. Commercial application of the process would include an additional step to further upgrade the content to greater than 90% to produce dore for marketing, but otherwise the demonstration plant operations were representative of how commercial operations would operate.

Commissioning commenced on March 10, 2011 and operations ran until August 19, 2011. During this period a total of 157 tonnes of dry copper plant residue was processed producing approximately 54 troy oz. of gold and 53 troy oz. of silver to electrowinning sludge. The campaign was divided into three periods as shown in Table 1.

Table 1 - Demonstration Plant Operating Phases

Phase	Dates
Commissioning	March 10 – May 2
Optimization	May 3 – July 20
Demonstration	July 21 – August 19

The copper plant residue was produced from copper concentrate from the KGHM Robinson mine in Nevada which had been previously processed through the CESL Copper Process.

The plant achieved high precious metals extraction. Precious metal extraction results are shown in Table 2 and are compared with bench tests processing the same material.

Table 2 - Demonstration Plant and Bench Precious Metal Extraction Results

Demonstration Phase	Plant Extractions			Bench Extractions	
	Optimal	Average	STDEV	Average	STDEV
Gold	96.2%	91.0%	4.0%	93.6%	2.9%
Silver	82.6%	73.2%	9.0%	72.2%	8.2%

The optimal extraction results observed for the demonstration plant compared with the bench tests can be partially attributed to greater control over the cyanide additions in continuous operations. Each compartment of the pressure cyanidation vessel has a cyanide addition port that aids in maintaining a constant active cyanide concentration throughout the leach. Furthermore, additional optimization testwork performed in 2016 improved silver extraction to greater than 90% under optimal conditions.

During the campaign the AVR circuit processed 150,000 liters of barren process solution at a flowrate of 3.7 L/min. Results from the novel application of AVR technology are described further below.

PLANT OPERATIONS

AVR Process Description

The purpose of the AVR circuit is threefold: 1) To maintain copper balance, liberate cyanide from copper complexes and recover the precipitated copper to the copper plant; 2) To recover and recycle cyanide to the Pressure Cyanidation circuit; and, 3) To maintain the water balance and send a low-cyanide bearing stream to cyanide destruct.

Copper enters the gold plant as soluble copper in entrained solution in the residue as well as leachable copper in the copper plant residue itself. To maintain a steady copper balance, an equivalent amount of copper must be removed from the gold plant. This is accomplished by acidification, enabling the copper to be precipitated and recycled to the copper plant. Many metal-cyano complexes, including copper-cyano complexes, are Weak Acid Dissociable (WAD), meaning they dissociate in weak acid solutions to form hydrocyanic acid (HCN) and a metal precipitate. In the case of copper, a CuSCN or CuCN precipitate will form when the stream is acidified. As SCN is present in solution, CuSCN precipitation is preferable to CuCN since the latter results in additional unrecoverable cyanide loss. Copper thiocyanate is favoured as a product when there is a sufficient concentration of thiocyanate as is the case for the CESL Gold-Silver Process.

After acidification, a portion of the stream is fed to the stripper column to recover cyanide contained in this stream prior to bleeding the solution to the cyanide destruct circuit to control the water balance. Cyanide recovery is accomplished using volatilization. The other portion of the acidification product stream is neutralized with caustic (NaOH), and split between recycling back to pressure cyanidation as feed liquor, and feeding the absorber column.

AVR Equipment Description

During the demonstration plant operations, after acidification the resulting slurry was fed to a 0.9 meter diameter thickener. The thickener underflow was sent to an underflow tank and then neutralized and the copper byproduct solids pumped into barrels. The thickener overflow solution was fed to the stripper and absorber columns. The actual columns are shown in Figure 3.

Figure 3 - Demonstration Plant AVR Circuit Absorber (right) and Stripper (left) Columns

Each column had a diameter of 0.6 meters. The stripper and absorber column heights were 6 meters and 5.5 meters respectively. All equipment was sealed and maintained under negative pressure and the ventilation stream was scrubbed with caustic to recover cyanide. The entire circuit was contained within a bermed and ventilated room with high air turnover supplied by overhead fans and louvers around the lower perimeter.

The stripper product solution was sent to the cyanide destruct circuit and the absorber product was sent back to the pressure cyanidation circuit as shown in Figure 4.
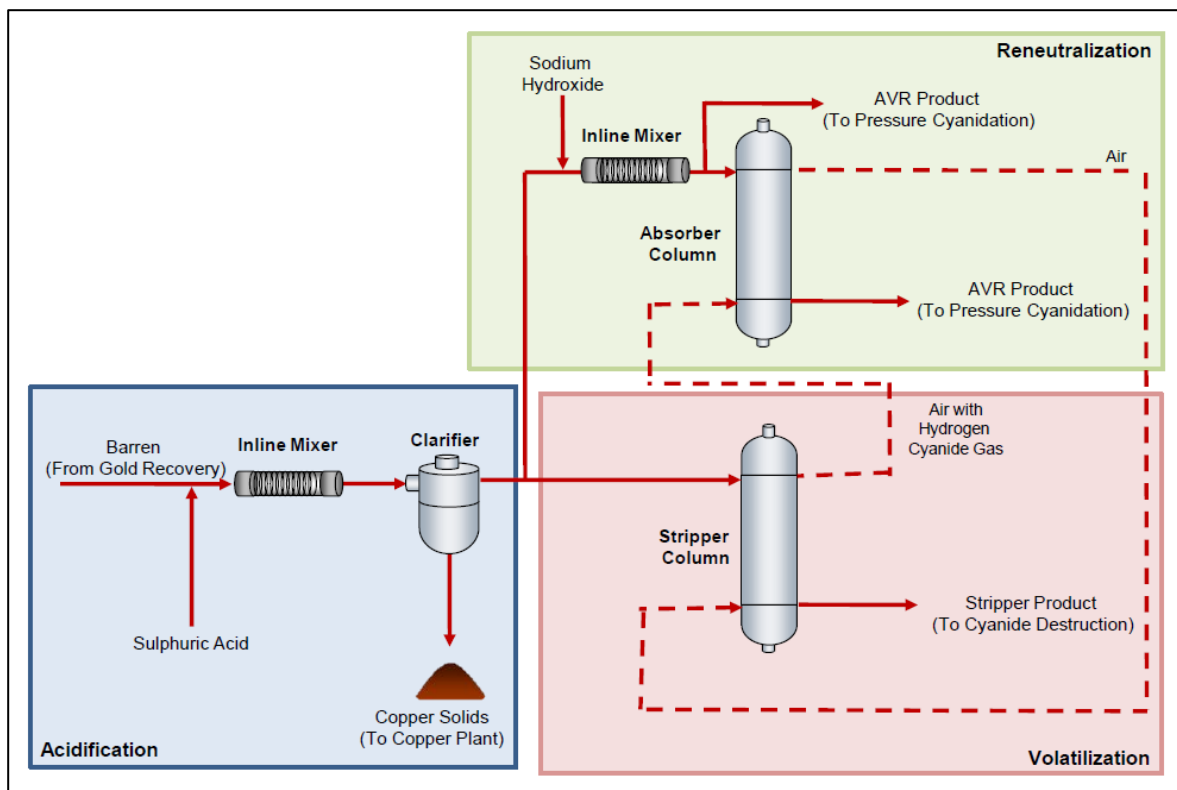
Figure 4 - AVR Circuit Flowsheet

Although the copper solids were not processed during the campaign, the copper thiocyanate solids are a value-add byproduct that would be recycled or marketed in a commercial application. For integration of the CESL Gold-Silver Process with the CESL Copper Process the solids are recycled back to the Copper Process where the copper is recovered as cathode.

AVR Key Performance Indicators and Results

The three key performance indicators that were identified for the AVR circuit were copper removal, cyanide recovery, and cyanide concentration in the stripper product solution. High efficiency of copper removal helps minimize the required size of the AVR circuit by avoiding a need to process the solution multiple times. High cyanide recovery reduces the overall cyanide consumption and lowers reagent costs. Minimizing cyanide concentration in the stripper product reduces costs associated with the downstream cyanide destruct circuit.

Copper removal was calculated as the delta copper in solution entering and exiting the acidification circuit. Copper thiocyanate is very insoluble (K_{SP} $25^{o}C = 1.77 \times 10^{-13}$). Samples taken of the thickener overflow were filtered and the filtrate and solids neutralized with caustic to avoid hydrogen cyanide volatilization. The neutralization also dissolved the copper particles. The results indicated that copper that was not removed was due to fine particles exiting the thickener in the overflow solution. An average copper removal of 93% was achieved during the demonstration phase.

Cyanide recovery was calculated as the percentage of cyanide recovered from all of the outlet streams versus the amount fed to the AVR circuit. Using this method, cyanide recovery included cyanide deporting to the stripper product. However, this cyanide was not recycled back to pressure cyanidation and so represents a loss and was further subtracted to calculate the true cyanide recovery. Cyanide losses were predominantly due deportment to the copper solids as copper cyanide as well as volatile cyanide losses. Other losses include oxidation byproducts of cyanide such as cyanate (CNO^-). An average total cyanide recovery of 93% was achieved during the demonstration phase.

The stripper product cyanide concentration was directly measured from the solution stream. An average stripper product concentration of 27 mg/L cyanide as weak acid dissociable (WAD) sodium cyanide (NaCN) was achieved during the demonstration phase.

Targets are shown against results in Table 3.

Table 3 - Key Performance Indicators: Results, Target, and Variability

Key Performance Indicator	Unit	Target	Data	STDEV
Copper Removal	%	>90	93	3
Overall Cyanide Recovery	%	>90	93	12
Stripper Product [NaCN]	ppm	<100	27	13

VARIABLES AFFECTING KEY PERFORMANCE INDICATORS

Data was gathered for a large number of variables over the 5 month campaign for all of the circuits that were operated. The remainder of the paper focuses on key variables that had a meaningful impact on the AVR circuit performance.

Acidification pH and Solution Thiocyanate Concentration

One of the metallurgical objectives was to determine the optimal operating acidification pH to obtain the highest copper thiocyanate and lowest copper cyanide content in the acidification solids while achieving high copper removal. Based on the cyanide metal complex precipitation versus pH graph as shown in Figure 5, a pH of 2 is sufficient to remove over 95% of the metal from the anionic cyanide complex in solution (Lorosch, 2001). While this represents a good indication of where the optimal pH is, the graph represents ideal conditions and the complex nature of the barren solution composition undoubtedly affects the final outcome for copper removal.
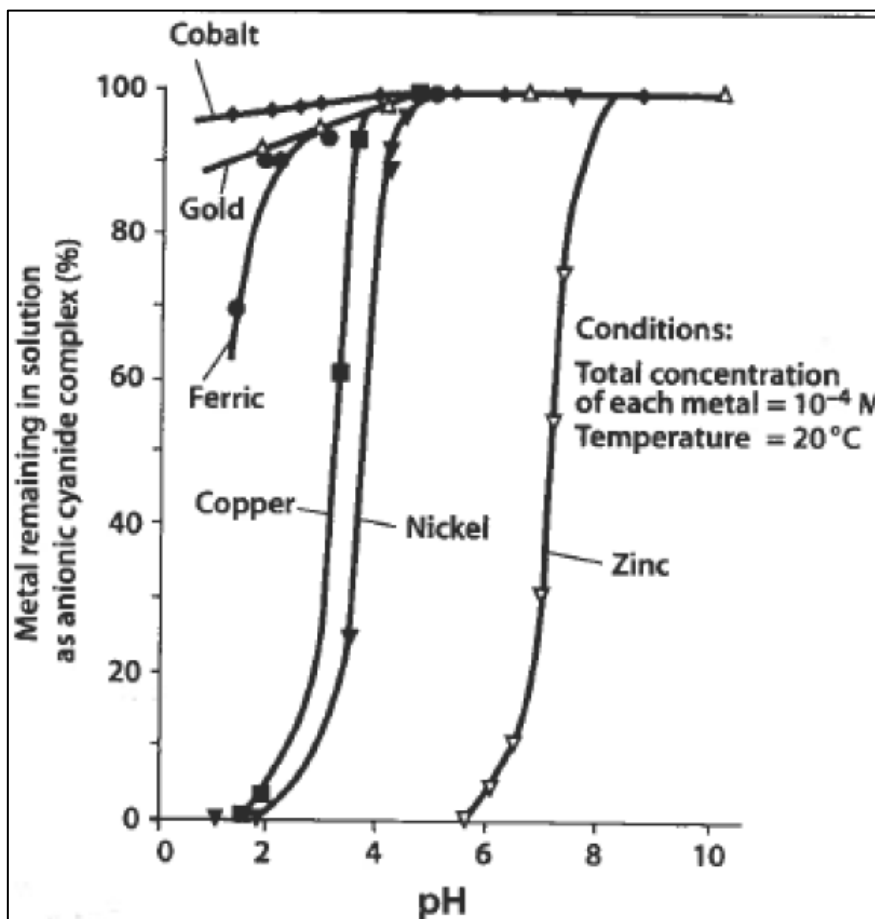

Figure 5 - Cyanide Metal Complex Precipitation vs. pH

Bench testing indicated that the optimal operating acidification pH was 2 to precipitate the maximum copper thiocyanate as shown in Table 4. There were no significant differences in the solid assays for acidification pHs of 1 through 3. However, at a pH of 4, the copper thiocyanate content decreased and the copper cyanide increased. The balance was not perfect for these tests but the results were indicative of a trend.

Table 4 – Acidification Solid Assays from Bench Testwork

	pH 1.0	pH 2.0	pH 3.0	pH 4.0
CuSCN (%)	96.5	100	94.9	70.6
CuCN (%)	3.4	2.9	3.5	7.7

A lower pH is advantageous in ensuring precipitation of copper and improved stripper efficiency by driving off volatile HCN. However, a lower pH increases costs associated with acid consumption to lower the pH as well as the necessary caustic to bring the pH back up after. Furthermore, it is not only important that the copper precipitates, but in what form the copper precipitates. Copper precipitation is discussed further below. Testing focused on identifying a pH that minimized the acid additions required while maximizing copper precipitation and minimizing copper cyanide in the precipitate.

During the Demonstration phase, a pH of 2 – 3 was found to produce copper solids with a CuCN concentration of 1% or less while still maintaining stripper efficiency. However, another sample of solids taken during acidification operations using a pH of 3 resulted in 6.9% CuCN in the solids. Further investigation was performed to correlate the amount of copper precipitated as copper thiocyanate with the ratio of copper to thiocyanate in solution. The copper cyanide composition in the acidification solids are shown in table 5.

Table 5 - Thiocyanate to Copper Ratio on Copper Cyanide Precipitation at Varying pHs

	pH 2.0	pH 2.5	pH 3.0	pH 3.0
CuCN (%)	0.32	0.5	1.0	6.9
SCN:Cu Ratio in Feed Solution	5.2	8.6	6.0	2.0

There were minimal differences in the copper cyanide content in the acidification solids for acidification reactor pH values 2 through 3 when the thiocyanate to copper ratio was above five. However, with the thiocyanate to copper ratio at two, there was an increase of copper cyanide in the solids at a pH of 3 which indicates that, if there is sufficient thiocyanate, the majority of the copper will precipitate out as copper thiocyanate. The thiocyanate to copper ratio in solution is predetermined by the extent of leaching in the pressure cyanidation circuit. Operation at the demonstration scale led to the development of operating strategies that respond to the measured ratio leading to potential savings for commercial operations.

The results of copper precipitation at various operating acidification pH values are shown in table 6. During the Optimization phase, the maximum copper precipitation occurred at an acidification pH of 2.5 which was subsequently used during the Demonstration phase.

Table 6 - Copper Precipitation Results

	pH 2.0	pH 2.5	pH 3.0	pH 2.5
Phase	Optimization	Optimization	Optimization	Demonstration
Copper Precipitation (%)	87.4	88.5	81.5	86.8
STDEV (%)	6.1	6.7	8.1	7.4

Copper precipitation was measured by assaying the solution immediately exiting the acidification inline mixer whereas copper removal was measured by assaying the solution immediately exiting the AVR thickener. The measured copper removal of 93% for the Demonstration phase indicates that a small amount of additional copper precipitated during the retention time in the thickener.

Volatilization pH

The circuit was designed with the capability to add additional acid to the stripper feed solution to operate the stripper at a lower pH than the acidification circuit. The driving force of lower pH on hydrogen cyanide volatilization is shown in the data correlating the stripper efficiency with feed solution pH in Figure 6.
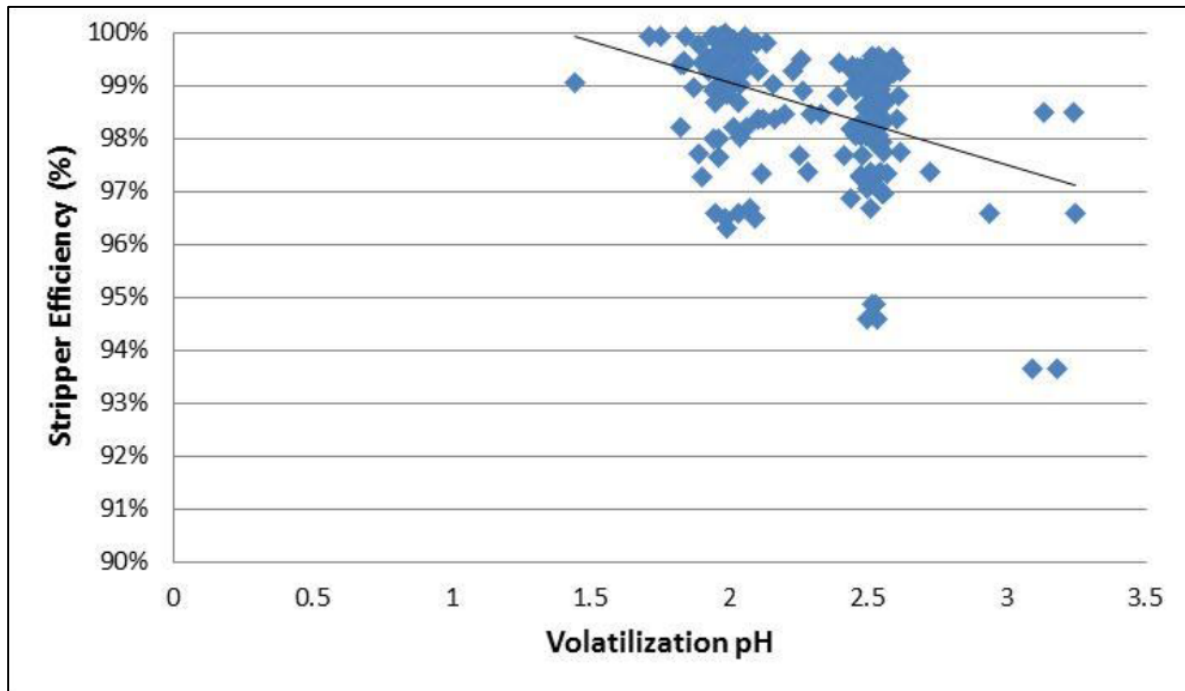
Figure 6 - Effect of Volatilization pH on Stripper Efficiency

Having an additional pH reduction downstream of the acidification thickener increased scaling in the stripper as well as caustic consumption in the reneutralization circuit and was ultimately abandoned as an operating practice.

Stripper and Absorber Airflow

The air to liquid ratio (volume:volume) is an essential parameter for mass transfer in the HCN stripper column. Typically, an air to liquid ratio of 600:1 is required for efficient volatilization. For the demonstration plant, the stripper height was shortened to accommodate the facility's ceiling limit and the air to liquid ratio was increased ten times to compensate in order to achieve high stripper efficiency. The original stripper air to liquid ratio target was 6000:1. In general, increasing the air to liquid ratio will improve stripping but inhibits absorbing, while decreasing the ratio will have the opposite effect. The air was circulated between the stripper and absorber with a bleed to the scrubber to maintain negative pressure in the columns. The efficiency not only varies with air to liquid ratio but with type and size of packing, fluid properties, column diameter and the extent of liquid dispersion over the packing surface. The stripper air to liquid ratio target was varied from 2500:1 to 6000:1 during operations.

The correlation between the stripper efficiency and air to liquid ratio at a pH of 2 is shown in Figure 7. The stripper efficiency increased with the air to liquid ratio and thus increased the hydrogen cyanide gas mass transfer.
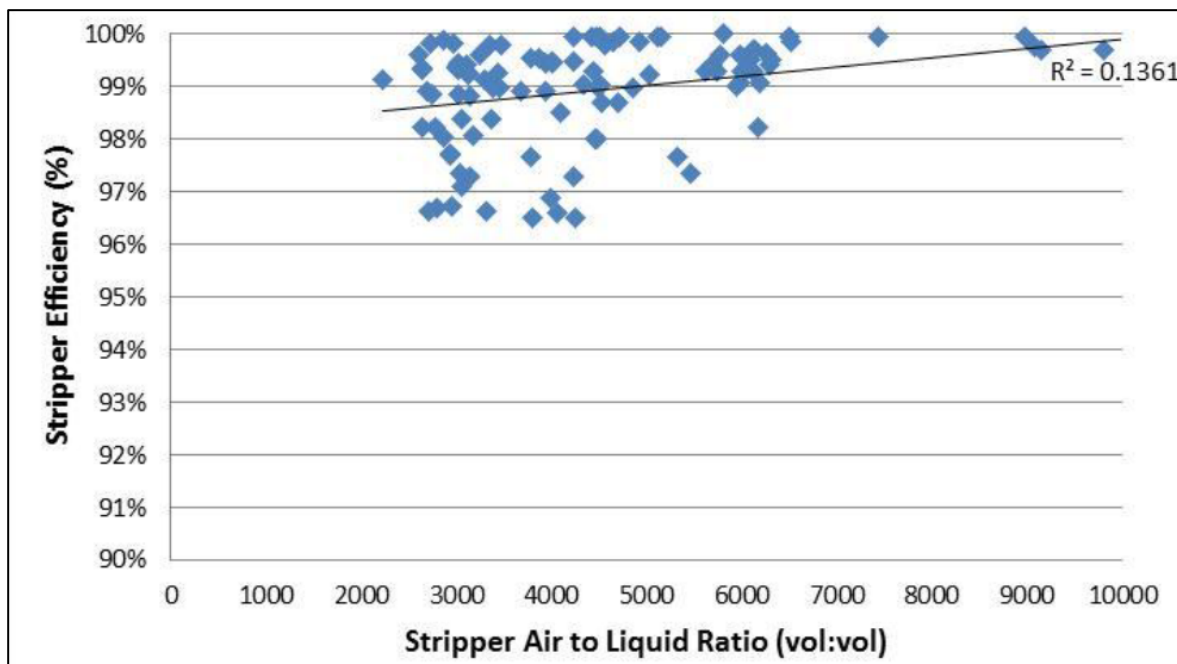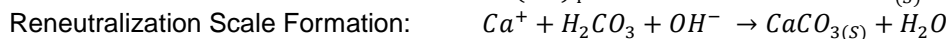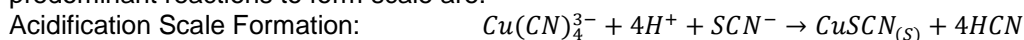
Figure 7 - Effect of Air to Liquid Ratio on Stripper Efficiency

Note that cyanide stripper efficiency, when the % efficiency calculation allows for up to 1mg/L cyanide in the stripper product, can essentially be operated at 100% efficiency. The cyanide losses to the stripper product represent less than 1% of the cyanide losses in the circuit but, more importantly, have implications on the cyanide destruct circuit. Achieving cyanide concentration targets for discharge to a tailings pond in the stripper product through operation of the stripper alone would save the cyanide destruct circuit reagent costs associated with cyanide removal. While the reagent costs of the cyanide destruct circuit might be eliminated, it was recommended to still have the circuit in place to improve overall operations and process flexibility.

OPERABILITY

Scaling

Operability of the AVR circuit was challenging during the commissioning phase due to scale buildup in the re-neutralization portion of the circuit. Scale formation is unavoidable in both the acidification and reneutralization circuits within AVR due to the large changes in pH. Scale formation was significantly less after the commissioining phase when better pH control was established. The two predominant reactions to form scale are:

Acidification Scale Formation: $Cu(CN)_4^{3-} + 4H^+ + SCN^- \rightarrow CuSCN_{(S)} + 4HCN$

Reneutralization Scale Formation: $Ca^+ + H_2CO_3 + OH^- \rightarrow CaCO_{3(S)} + H_2O$

Descaling of the AVR circuit was conducted after the commissioning phase and again at the end of the campaign. The inline mixers were weighed to quantify scale formation on a mass basis for the Demonstration phase. The absorber feed reneutralization inline mixer experienced the greatest scale formation as shown in Table 7.

Table 7 - Scale Formation Rates in AVR

Parameters	Acidification	Volatilization	Reneutralization (to PCN)	Reneutralization (to absorber)
pH	2.0	2.0	10.5	12.8
Scale Composition	CuSCN	CuSCN	CaCO$_3$	CaCO$_3$
Quantity (mg / L solution)	2X10^{-4}	2X10^{-4}	2X10^{-3}	3
Descaling Reagent	NaOH	NaOH	HCl	HCl

Two percent caustic solution was effective in descaling the acidification solids. Hydrochloric acid was effective in descaling calcium carbonate in reneutralization. Eighteen percent hydrochloric acid was found to be an effective concentration to descale the reneutralization process lines.

AVR operated with 98.3% availability. Availability for the AVR circuit was defined by the acidification runtime. Downtime was predominantly caused by plugging caused in the reneutralization circuit due to calcium carbonate scale. With scale growth rate quantified, scheduled downtime must occur at regular intervals to maintain circuit operability. Secondary sets of piping can be used to minimize the impact on circuit availability.

CONCLUSIONS

The demonstration plant operated for 5 months to obtain sufficient data to reduce scale up risk of the CESL Gold-Silver Process. No issues were identified that could not be addressed through normal operating and maintenance practice and key design criteria were gathered for application at commercial scale.

The AVR circuit achieved above target results for the identified key performance indicators. Cyanide recovery in the CESL Gold-Silver Process flowsheet using AVR was successfully demonstrated for continuous operations. The process was proven to operate safely and efficiently while achieving all metallurgical objectives.

ACKNOWLEDGEMENTS

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