Copper and cyanide recovery from barren leach solution at the gold processing plant

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ABSTRACT

As easily mined gold deposits are becoming increasingly rare, gold producers are turning to the processing of ores with polymetallic and copper mineralization. These base metals can create metallurgical and waste handling/disposal challenges, which can render the project uneconomic. Base metals such as copper compete for the cyanide reagent used to extract gold, necessitating the need to increase cyanide volumes and consequently, cyanide consumption costs. Copper will also stabilize in tailings water as weak acid dissociable cyanide, a form that is both difficult and costly to destruct.

SART (sulphidization-acidification-recycling-thickening) process technology can be applied to remove base metal interferences in gold projects. SART breaks the copper-cyanide complex and precipitates the copper as a saleable copper sulphide concentrate. With the copper removed, the cyanide can be regenerated as free cyanide for recycle to the gold recovery process. This improves cyanide utilization efficiency and mitigates copper presence in tailings. Additionally, copper recovery generates an incremental revenue source to further improve project economics.

Engineering Dobersek GmbH together with BioteQ developed a SART and AVR testing program to recover cyanide and maximize operational efficiencies at a gold processing plant in Kazakhstan with high cyanide consumption in the leach circuit. Results from on-site testing demonstrated that up to 99.98% of copper can be removed and precipitated as copper sulphide and 60–90% of cyanide can be recovered from the AVR and recycled for leaching, reducing total overall cyanide use. This paper provides an overview of the testing methodology and results together with a discussion on the potential of SART to improve gold production operations to deliver both environmental and economic benefits.

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INTRODUCTION

Located in the Republic of Kazakhstan, the gold mine processes 8 million tons of Run of Mine (ROM) ore annually. The mine produces an arsenopyrite concentrate that is processed with a Leachox procedure consisting of ultra-fine grinding, followed by pre-oxygenation leach tanks together with Aachen reactors. The pre-oxygenated feed is directed to the recovery of the dissolved gold through a carbon-in-pulp (CIP) circuit with the gold leaching procedure taking place in a leach column. A simplified block flowsheet of the overall process is provided below:
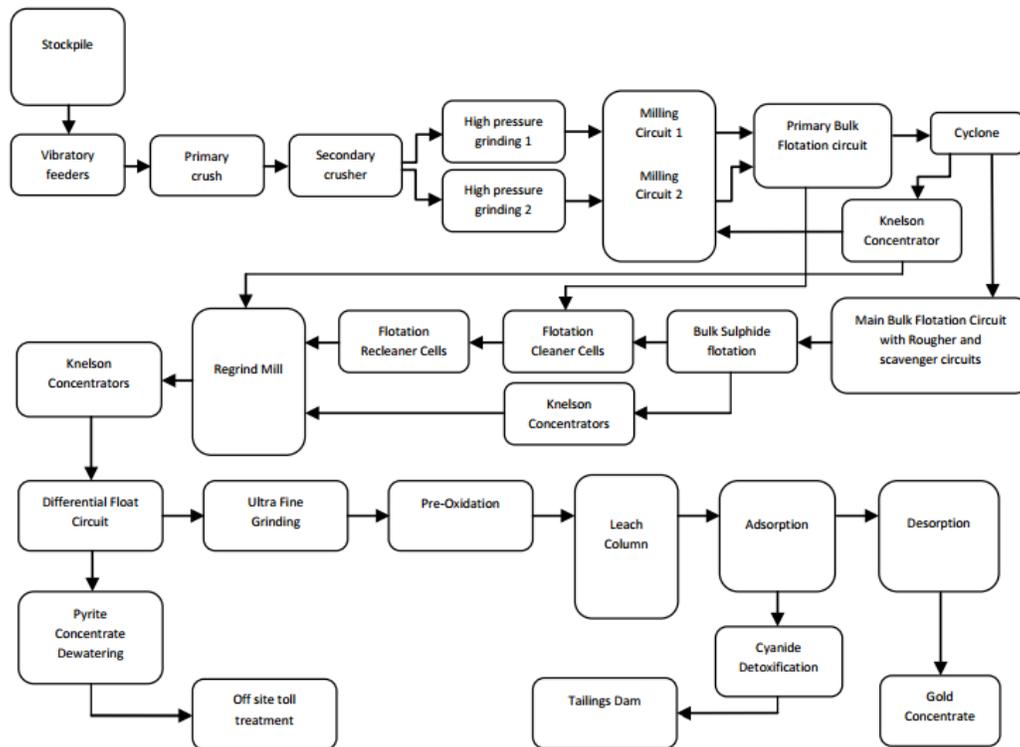
Figure 1 Simplified gold mine flowsheet

Problems created by CN-soluble copper in leach solution

Copper contamination of gold cyanidation circuits causes a number of problems in gold processing (Sceresini, 1999). Copper oxide minerals (i.e. azurite, malachite, cuprite, tenorite) have fast leaching rates in cyanide. Secondary copper sulphide minerals such as chalcocite and covellite leach rapidly in cyanide while more refractory copper sulphides such as chalcopyrite, cubanite, and enargite leach considerably slower in cyanide (Adams, 2000). As a result of cyanide soluble copper in the ore, cyanidation of gold-copper ores results in high cyanide consumptions and difficulty in process control.

The gold leaching reaction in cyanide solution follows these electrochemical half-reactions:

| Anodic: | $Au + 2CN^- = Au(CN)_2^- + e^-$ | (1) |
| Cathodic: | $O_2 + 4H^+ + 4e^- = 2H_2O$ | (2) |
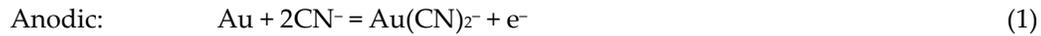
Cyanide forms a series of complexes with several metals. In the case of copper the following chemistry applies, where x ranges from 1 to 4:

$$Cu^+ + xCN^- \leftrightarrow CuCN_x^{-(x-1)} \qquad (3)$$

In order to effectively leach gold, sufficient free cyanide must be present. Large amounts of cyanide-soluble copper can rapidly decrease the available cyanide far below the levels required, resulting in unleached gold in tailings solids or heap leach residues. Moreover, there is evidence that under these cyanide deficient conditions, soluble gold is adsorbed back on to copper minerals by reduction onto surface defect sites, again resulting in loss to tailings (Adams, et al., 1996).

A general operating principle for the leach is to maintain a molar ratio of added CN:Cu of no less than 4 and preferably over 5. The use of a cyanide auto-analyser or more frequent cyanide titrations is required to achieve this. In cases where there is a large amount of cyanide-soluble copper such as an intensive leach constant high cyanide addition is required. In such cases, copper levels of ~1,000 mg/L have been observed.

Adsorption of copper cyanide complexes on to activated carbon in the adsorption stage for gold recovery follows the trend show below:

$$Cu(CN)_2^- > Cu(CN)_3^{2-} > Cu(CN)_4^{3-} \qquad (4)$$

The predominance of the $Cu(CN)_2^-$ complex under cyanide deficient conditions is yet another reason to maintain excess free cyanide in the leach. By avoiding copper in solution, gold is more effectively loaded on the carbon rather than being displaced by copper. Moreover, excess copper in the eluate reduces electrowinning cell efficiency, resulting in copper-contaminated doré bullion.

Measures such as selective mining are often not applicable, given that gold and copper mineralization is often concurrent in these ores. Chemical means of removing reactive copper, such as acid leaching, are generally not economic. Alternatives include the addition of ammonia to the cyanide leach to suppress copper leaching (Hunt, 1901; Muir et al, 1995; Drok & Ritchie, 2000); this option has only seen minor application (Butcher, 1995) and is reported to be difficult to control in practice. Copper mineral dissolution can be suppressed by means of surfactants such as fatty alkyl amines (Bennett et al, 1991), which passivate the copper mineral surfaces, thus reducing copper dissolution. There may also be a reduction in gold leaching, however.

Application of SART/AVR within the existing flow sheet

Prior to SART treatment, solids are removed from the solution with a target of 100 ppm TSS or less. Current process options include counter current decantation (CCD) and natural settlement within existing tailings pond.

The liquid free of solids represents the feed into the SART plant, where the recovery of the copper and silver (in the form of Cu_2S and Ag_2S as filter cake) takes place. The next process step involves treatment of the solution within an acidification, volatilization and recovery (AVR) circuit in order to recover the cyanide in the form of NaCN. Subsequent to the filtration, the remaining liquid is essential for the removal of impurities and the extraction of gold within an Ion Exchanger plant.

Any surplus liquid can be mixed with the washed solids from the previous stage of solid-liquid separation and can be pumped to the existing tailings pond in order to be exposed to natural ultraviolet (UV) degradation of the remaining cyanide.
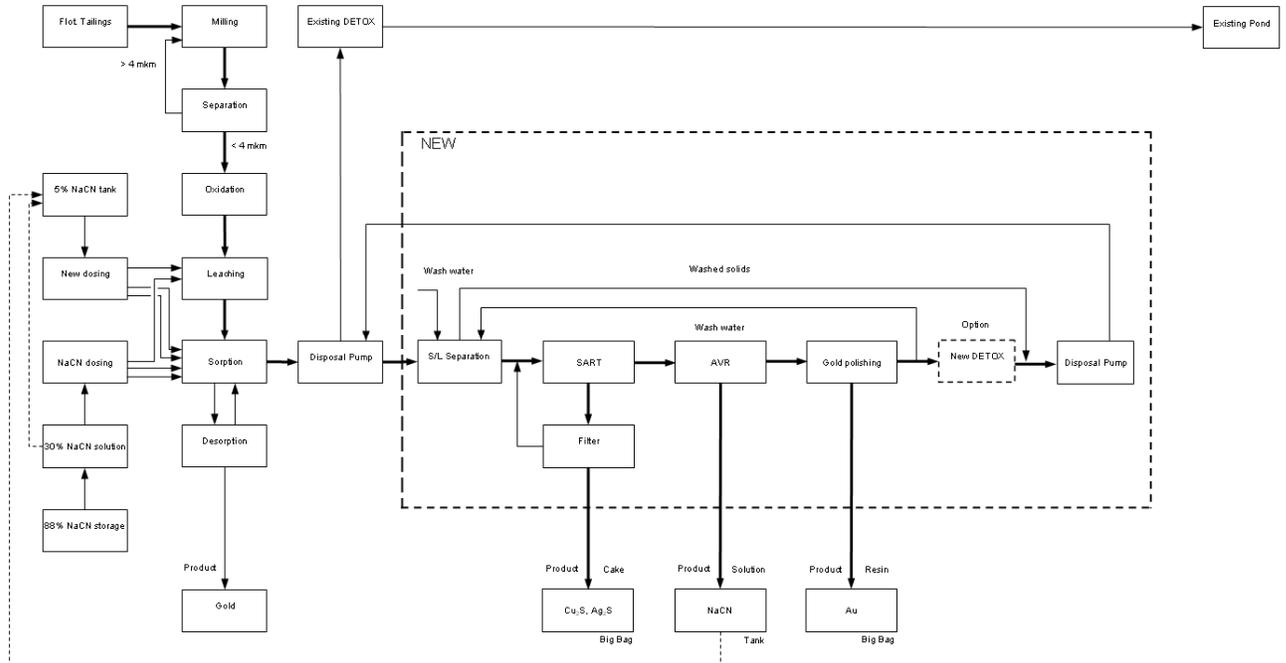
Figure 2 SART/AVR after S/L separation by Counter Current Decantation (CCD)

Technical feasibility of SART/AVR process

Proposed SART and AVR stages were tested in a bench scale onsite, according to the following arrangement:
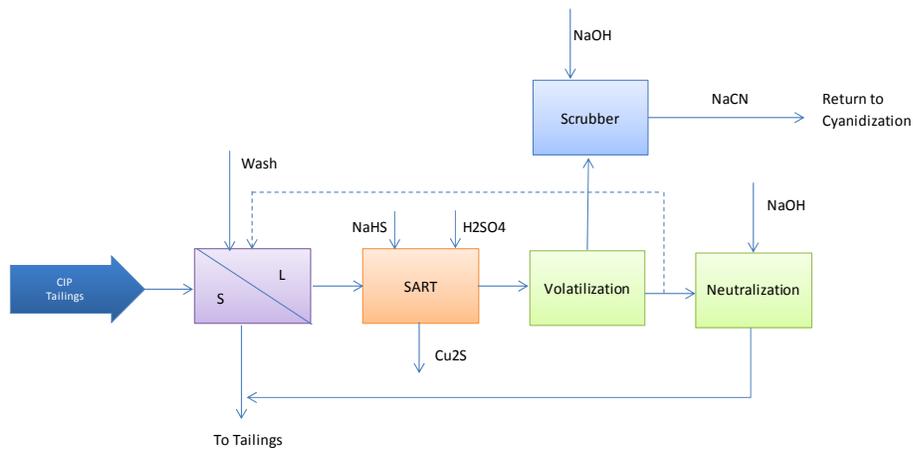
Figure 3 SART/AVR test arrangement

Solid-liquid separation: to separate the solution from the solids in the CIP tailings. This process step will likely include CCD and a wash stage to maximize the recovery of cyanide, copper and silver. Solids underflow from the CCD circuit will be sent to the final plant tailings via the existing cyanide detoxification circuit.

SART: to acidify the tailings solution to recover the dissolved copper as Cu_2S with the addition of NaHS. Other weak acid dissociable (WAD) cyanide complexed metals and arsenic are also expected to be precipitated as sulphides.

Volatilization (AVR): for water balance purposes it will be necessary to concentrate the cyanide in the SART effluent by first volatilizing the cyanide from the acidic solution, and then capturing the liberated cyanide in a lime (or caustic) scrubber to produce $Ca(CN)_2$ (or NaCN) for recycle to the leaching circuit.

Neutralization: the final stage of processing involves adjustment of the pH of the AVR effluent solution prior to mixing with the high density tailings for tailings disposal.

METHODOLOGY

The primary objective of the experimental work was to characterize the performance of the SART process with respect to key operating parameters such as copper recovery, cyanide regeneration, reagent consumption and final plant effluent quality. In addition, the deportment of other elements in the feed solution (*e.g.* As) was assessed. The outcome of the experiments determined the SART process conditions that yielded the best combination of heavy metal recovery and free cyanide regeneration from WAD cyanide. Each SART/AVR experiment was conducted sequentially in two stages, copper precipitation followed by AVR stripping/absorption.

The barren leach solution (BLS) feed for the entire test program was prepared by filtrating 10 litres of slurry from the CIP tailings. Five litres of the filtrated solution were used as a feed for all tests. A sample of this feed solution was taken prior to the testing in order to have a full chemical characterization of feed.

Assays for ICP-metals, gold, cyanide speciation and anions were required of the feed and effluent for each experimental run, as outlined in below:

- In-reactor measurements: pH, oxidation-reduction potential (ORP)

- NaHS strength: Cu

- Solution assays (SART feed and effluent): Cu, Au, Ag, free CN

- Solution assays (AVR feed and effluent): free CN

Sulphidization/Acidification

SART tests were conducted in batch mode, where the copper precipitation was accomplished in two stages: Acidification and Sulphidization.

Acidification is needed in order to break the WAD bond between Cu (and other WAD metals) and CN in an acidic environment. An acid solution of H_2SO_4 10 % w/w was used.

$$Cu(CN)_4^{3-} + 4H^+ = 4HCN + Cu^+ \tag{5}$$

After the WAD bond is broken, a sulphide source allows the copper to be precipitated as Cu_2S combined with other elements in a sulphide environment (*e.g.* As). A NaHS solution of 5 % w/w was used.

$$2Cu^+ + HS^- \rightarrow Cu_2S_{(s)} + H^+ \qquad (6)$$

$$2H_2AsO_3^- + 3HS^- \rightarrow As_2S_{3(s)} + 5OH^- + H_2O \qquad (7)$$
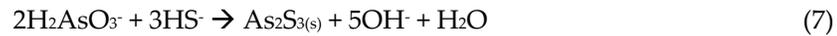
The key process parameters in the copper precipitation stage are pH and ORP. During copper precipitation, BLS was added, then acid and NaHS solutions were transferred into the SART contactor. All tests were mixed in batch for 9-11 minutes. Solid black-colored precipitates formed very quickly following addition of the sulphide reagent, illustrating that the SART reactions occur well within the 9-11 minutes of contact time used.

After reaching the required pH (4.0 for all testing) and ORP (variable, depending on Cu stoichiometric consumption), a flocculant solution (12 gpl) was added in order to achieve a flocculant concentration of 20-25 ppm in solution. The flocculated slurry from the contactor was filtered, and the liquid filtrate saved for AVR testing.

Nine SART experiments were performed at pH 4.0, at varying NaSH dosages as follows:

- 3 experiments at NaHS dosage of 100% of Cu stoichiometric

- 3 experiments at NaHS dosage of up to 120% of Cu stoichiometric

- 3 experiments at NaHS dosage of 105% of Cu+As stoichiometric (equivalent to 330% Cu stoichiometric).

Acid Volatilization Recycling (AVR)

In this batch/non-steady state volatilization test, the evolution of HCN from the SART effluent could be related to the solution pH (free acidity) since both liquid-gas and HCN/CN equilibria occur simultaneously.

$$HCN_{(g)} = HCN_{(aq)} \qquad (8)$$

$$HCN_{(aq)} = CN^- + H^+ \qquad (9)$$

Three AVR experiments were performed, each with a duration of 120 min. Solution samples from the AVR vessel and scrubber were collected at the end of each test.

At the end of each SART run, the pH of the solution was raised to 12 with a 20 wt% NaOH solution in order to minimize HCN losses prior to the start of the AVR experiments. Neutralized solution from SART experiments #1-6 were mixed to generate the AVR feed. Prior to the AVR testing, the alkaline feed solution was acidified from pH 12 to pH 3.5-4.0 using 10 wt% H_2SO_4 solution. After each AVR test, the pH of the AVR effluent (spent solution) was raised from pH 4.2-4.3 to pH 11.0 using 5wt % NaOH solution.

TEST RESULTS

The results of the nine SART experiments are summarized in Table 1 below.

Table 1 SART results summary

Test ID	pH	NaHS	Acid	NaHS	Cu(*)	As(*)	Free CN(*)	Cu recovery	As removal	CN-WAD recovery
-		Cu stoich %	kg/m³	kg/kg Cu	mg/L	mg/L	mg/L	%	%	Theoretical %
SART Feed	10.70	-	-	-	95.35	81.80	771.0	-	-	-
SART 1	3.90	120	2.13	0.50	1.07	55.60	860.0	98.9	30.5	98.9
SART 2	4.24	120	2.13	0.50	0.90	43.40	644.6	99.0	45.7	99.0
SART 3	4.10	120	2.13	0.50	1.48	64.80	676.9	98.4	19.0	98.4
SART 4	4.05	100	2.13	0.41	7.66	66.40	805.9	91.8	17.0	91.8
SART 5	4.22	100	2.13	0.41	8.99	68.00	741.4	90.4	15.0	90.4
SART 6	3.93	100	2.13	0.41	9.08	70.40	752.1	90.3	12.0	90.3
SART 7	4.21	330	2.20	1.38	0.25	72.00	-	99.7	9.8	99.7
SART 8	4.22	330	2.17	1.38	5.95	69.20	-	93.6	13.3	93.6
SART 9	4.19	330	2.17	1.38	201	42.60	-	97.8	46.6	97.8

(*) Cu, As, Free CN assays has been modified according the dilution factor used for each test

NaHS Addition

- SART 1-3: NaHS added was 120% of Cu stoich (0.419 ml)

- SART 4-6: NaHS added was 100% of Cu stoich (0.349 ml)

- SART 7-9: NaHS added was 105% of Cu+As stoich or 330% Cu stoich (1.159 ml)

For runs 7-9, the main objective was to explore the possibility of the complete precipitation of Cu and As in feed by using a NaHS excess. The measured high acid consumption was expected, given the high concentrations of free CN in the feed solution. The majority of acid consumed in the SART process (2.08 kg H_2SO_4/m³ feed) was due to a buffer effect produced at pH 8.5-9.5 due to high cyanide content in the feed solution.

Cu/As Removal Efficiency

- SART 1-3: Average Cu and As removal was 98.8% and 31.7% respectively. This result was expected based on the excess dosage of NaHS in these experiments.

- SART 4-6: Average Cu and As removal was 90.8% and 14.7% respectively. Lower recoveries were expected since the NaHS dosages were lower (100% of theoretical stoichiometric based on Cu) and other species present in the feed solution could have reacted with the sulphide reagent (*e.g.* other WAD metals, As).

- SART 7-9: Average Cu and As removal was 97.1% and 23.2% respectively. The relatively high recovery of Cu was expected, given the excess NaHS dosages added. The relatively low %

removal of As suggests that a portion of the As was present in the feed solution in an oxidized state which may remain soluble upon sulphidization (*e.g.* As(V)).

CN Recovery

Recovery of CN associated with WAD metal complexes can be estimated theoretically based on the dissolved WAD metal assays, the majority of which are Cu, Zn, Ni and Ag.

$$CN_{Rec}\% = \frac{(Cu_t - Cu_f) \cdot 4 \cdot \frac{26}{63.5} + (Zn_t - Zn_f) \cdot 4 \cdot \frac{26}{65.4} + (Ni_t - Ni_f) \cdot 4 \cdot \frac{25}{58.7} + (Ag_t - Ag_f)}{CN_{WAD-t}} \quad (10)$$

Using NaHS dosages of 120% of Cu stoich, WAD cyanide recovery from the feed could be as high as 98-99%. This can be translated into an increase in CN-free from 771 ppm up to 931 ppm at the SART discharge.

Sulphide Solid-Liquid Separation

Solid-liquid separation of precipitated Cu_2S was effective with the use of Aluminex 20 flocculant, resulting in an easily distinguished settled solid phase. However, detailed solid-liquid separation characterization was outside the scope of this program. In BioteQ's experience designing and operating full scale SART plants, production of high-grade, saleable sulphide precipitate with good settling and filtration characteristics requires careful selection of flocculant and flocculant dosage, solid seeding rate, and reagent injection system.

AVR Test Results

The results of the three AVR experiments are summarized in Table 2 below.

Table 2 AVR results summary

Test ID	pH Initial/final	Free CN (*) Stripping	Free CN (*) Absorption	CN recovery Stripping Stage	CN Recovery Absorption Stage
-		*mg*/L	*mg*/L	%	%
AVR Feed	12.01	590.96	-	-	-
AVR 1	3.31 / 3.47	361.65	226.95	38.8	91.1
AVR 2	3.66 / 4.50	427.14	126.40	25.3	71.1
AVR 3	3.62 / 4.18	377.61	173.30	34.1	72.3

(*) Free CN assays has been modified according the dilution factor used for each test

For all AVR stripping experiments, the free CN concentration decreased after two hours, with an average CN removal in the stripping step of 32.7%. The relatively slow rate of CN stripping measured in the bench-scale apparatus was expected since the experiments were completed batch mode (non-steady-state). In the batch experimental procedure, higher recoveries of HCN were expected during the first minutes of testing due to the high concentration driving force between the liquid and gaseous phases. However, as the HCN concentration in the liquid phase drops, the mass

transfer driving force drops over time, reducing the rate of HCN stripping over time. The reduction in the rate of HCN stripping can be seen in the reduction in the gradient slope of the Free Acidity vs. time over the duration of the AVR experiment, as shown in Figure 6.
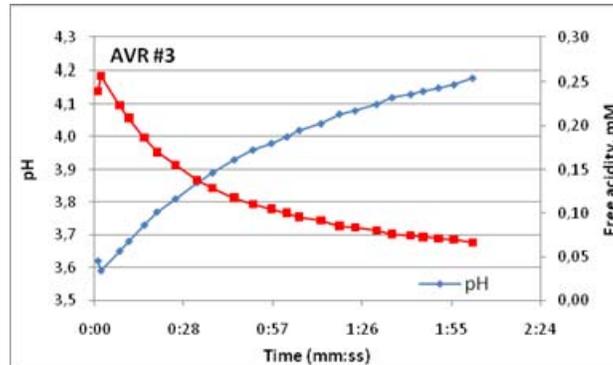
Figure 4 pH/H+ evolution during AVR run # 3

The average NaOH consumption in this final effluent neutralization step was 0.842 kg NaOH/m^3 spent solution, which is consistent with the theoretical NaOH requirement of 0.835 kg NaOH/m^3 spent solution. If cyanide stripping of 80% is achieved, then the expected NaOH consumption will drop to 0.36 kg NaOH/m^3 spent AVR solution.

An average CN recovery of 78.7% was measured in the adsorption stage of AVR, which was lower than expected. From previous experience, very high CN recoveries of nearly 100% were expected in the caustic scrubber, since cyanide absorption in caustic solution is dominated by the chemical reaction kinetics rather than mass transfer and the neutralization reaction kinetics are known to be very fast at excess caustic concentrations.

CONCLUSIONS

Results on performed tests can be summarized as:

- As expected, the SART reaction kinetics are fast and a HRT of less than 10 min is required.

- An average of 99% recovery of Cu and 32% recovery of As was achieved at a NaHS dosage of 120% of Cu stoichiometric.

- Acid consumption was 2.13 kg H$_2$SO$_4$/m^3 BLS, as expected according to theory.

- Recovery of CN associated with WAD complexes can be estimated based on metals assays. Since Cu is the major WAD metal present, WAD cyanide recovery will be similar to Cu, achieving up to 98-99% recovery of CN-WAD.

- The observed CN removal in the stripping stage of AVR was relatively low, due to the non-steady state nature of the batch stripping experiments. Higher rates of HCN stripping were observed during the initial stages of each AVR experiment. A higher degree of cyanide stripping from 60-90% is expected in a commercial scale stripping column operating at continuous steady-state conditions.

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