Managing copper in leach solution at the Çöpler gold mine: laboratory testing and process design

M. Botz
Elbow Creek Engineering, Inc., Billings, MT

A. Kaczmarek and S. Orser
Alacer Gold Corporation, Turkey

Abstract

Alacer Gold Corporation is constructing the Çöpler Gold Mine in eastern Turkey. Mining commenced in the fourth quarter of 2009 and gold production started in the fourth quarter of 2010. The mine is a 15,500 t/day oxide heap leach with three-stage crushing, agglomeration, carbon adsorption and electrowinning for final metal recovery. Leach solution copper levels are expected to be relatively low during the first two years of production, but will increase in later years due to higher copper content in the mined and processed ore. Over the mine life, approximately 40 Mt of ore will be placed on the leach pad, which will contain about 35,000 t of copper. Metallurgical testing indicates copper extraction will vary by ore type and, if controls are not implemented, may lead to copper levels exceeding 1,000 mg/L in pregnant solution. High copper levels in leach solution have the deleterious effect of increasing cyanide consumption and potentially overwhelming the ability of the carbon circuit to effectively adsorb the principal economic metals, which in this case are gold and silver. Using data obtained from laboratory leach column testwork, the heap leach facility was modeled using METSIM process simulation software to estimate the build-up of copper in leach solution over the life of the mine. Laboratory testwork was also performed to evaluate process conditions for treating a portion of pregnant leach solution via sulfide addition to precipitate saleable copper as copper sulfide (Cu_2S).

Copper precipitation process description

Copper removal from cyanide leach solution can be accomplished through the addition of sulfide at acidic pH to precipitate copper sulfide as a solid. This approach to removing copper through sulfide addition has been known for over 50 years. There has been renewed interest in the process recently, due to the increasingly common issue of high copper levels in cyanide leach solutions. The term sulfidization-acidification-recycle-thickening (SART) has been recently coined as an acronym to identify the copper sulfide precipitation process.

At a pH of approximately 4.0 to 5.0, the addition of soluble sulfide to a copper-bearing leach solution will result in the precipitation of copper sulfide (Cu_2S) solid. The overall acidification and sulfidization reaction is (assuming the use of sulfuric acid for pH adjustment):

$$2Cu(CN)_3^{-2} + 3H_2SO_4 + S^{-2} \rightarrow$$
$$Cu_2S_{(s)} + 6HCN_{(aq)} + 3SO_4^{-2}$$
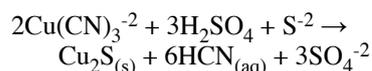
The above reaction is written relative to the copper-cyanide complex $2Cu(CN)_3^{-2}$, though analogous reactions also take place with the other common copper-cyanide complexes $Cu(CN)_2^-$ and $Cu(CN)_4^{-3}$. Sulfide in the above reaction (S^{-2}) is normally supplied as sodium hydrosulfide (NaHS) purchased in solid or liquid form. Other sources of sulfide such as hydrogen sulfide (H_2S) and sodium sulfide (Na_2S) would also suffice, but they may be more difficult to handle or be more expensive.

Two characteristics of this reaction that are beneficial to a leaching operation are:

1. Copper is removed from solution as Cu_2S solid, which can then be sold to a smelter for its copper value.
2. Cyanide that is complexed with copper in leach solution is released as free cyanide, thereby regenerating cyanide that can be recycled to the leaching operation for continued use.

In addition to copper, sulfide will react with the cyanide complexes of silver, cadmium, mercury and zinc to precipitate the respective sulfide solids. Though the gold-cyanide complex
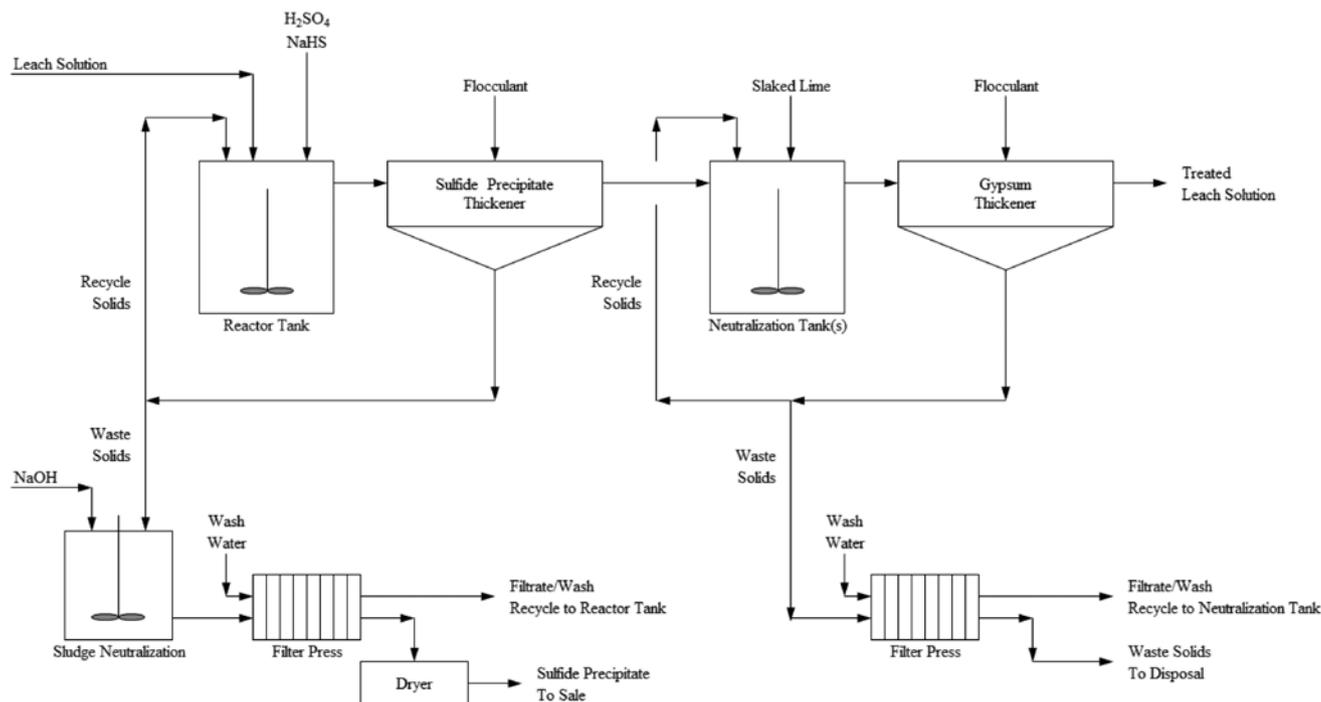
Figure 1 — Copper-sulfide precipitation process flow diagram.

is thermodynamically stable in this reaction environment, it has been observed that a small portion of gold is removed in the process, likely through sorption onto precipitated solids.

In a commercial SART plant, sulfuric acid and sodium hydrosulfide are added to copper-bearing leach solution to precipitate copper sulfide. The reaction rapidly proceeds to completion and precipitated solids are removed from solution in a thickener. To facilitate growth of copper sulfide crystals during the precipitation step, a portion of thickener underflow solids is normally recirculated into the untreated feed solution. The recirculation of the thickener underflow yields solids that settle more quickly and are readily filtered. Excess solids from the thickener underflow are neutralized, filtered, washed and then sold for metal values. Of particular note with these solids is the potential presence of silver and gold, which increase the value of the sulfide precipitate.

Acidic thickener overflow solution is neutralized to about pH 10.0 to 11.0 with lime to convert aqueous hydrogen cyanide to the non-volatile cyanide anion, according to the following reaction:

$$2HCN_{(aq)} + Ca(OH)_2 \rightarrow 2CN^- + Ca^{+2} + 2H_2O$$
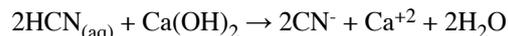
Due to the addition of sulfate in the acidification step and the addition of calcium in the neutralization step, calcium sulfate (gypsum) normally precipitates to some extent in the process. To promote gypsum precipitation in a controlled manner, a second thickener with solids recycle is typically incorporated into the neutralization step. The final solution from the SART process contains a low level of copper at a pH of about 10.0 to 11.0 with free cyanide that has been liberated (i.e., regenerated) from the copper-cyanide complexes.

A process flow diagram illustrating the sulfide precipitation steps is shown in Fig. 1. To prevent escape of hydrogen cyanide gas from the system, tanks containing acidic cyanide solution are covered and ventilated to a scrubber operated with sodium hydroxide. In some cases, drying of the sulfide precipitate may be required to reduce the moisture content to a level acceptable by the smelter receiving the material. For all applications, laboratory testing of the process with representative solution is recommended in order to determine reagent dosages, preferred operating pH, copper precipitation efficiency (or precipitation efficiency for other metals) and criteria for sizing thickeners and filters.

Copper precipitation process testwork

Batch tests. In February 2010, laboratory SART testwork was conducted using pregnant leach solution samples generated from a variety of ore samples collected from the Çöpler site. Both batch testwork and continuous throughput testwork were conducted to compare the performance of static versus dynamic test conditions. Pregnant leach solution samples were prepared to represent years three through nine of the planned heap leach operation, with these solution samples containing about 300 to 800 mg/L copper. Copper concentrations in each of the nine samples are listed in Table 1.

Twenty-seven small batch tests were conducted with 500-

Table 1 — Leach solution copper concentrations.

Sample code	Copper (mg/L)
Y3/7-300	311
Y4-300	301
Y4C-300	463
Y4-500	535
Y4-750	831
Y5-300	307
Y6-300	310
Y8-300	304
Y9-300	348

mL samples of each of the nine leach solutions listed in Table 1. The twenty-seven tests correspond to three tests at varying sulfide additions for each of the nine leach solutions. In all tests, the target reaction pH was 4.50 and the target sulfide dosages were 100%, 110% and 120% of the stoichiometric demand. The target reaction pH of 4.50 was selected based on earlier screening testwork that indicated copper precipitation was nearly complete at this pH.

Following the small-batch tests, larger batch tests were conducted with approximately 5-L samples in order to generate sufficient quantities of precipitated solids such that full elemental assays could be completed. Nine large batch tests were conducted with each of the samples listed in Table 1 at a target reaction pH of 4.50 and a target sulfide dosage of 120% of the stoichiometric demand.

For both the small- and large-batch tests, the test procedure consisted of the following steps:

1. A measured portion of leach solution was added to the reaction container. The solution was mixed either with a magnetic stirrer (small-batch tests) or an overhead stirrer (large-batch tests). The initial solution pH, oxidation-reduction potential (ORP) and temperature were recorded.
2. Sodium hydrosulfide solution was added to the sample according to the target stoichiometric dosage. A burette was used for the sodium hydrosulfide solution addition to ensure an accurate dosage.
3. Sulfuric acid solution was added to the sample to achieve a pH of about 4.50. A burette was used for the sulfuric acid solution addition to ensure the dosage could be accurately determined.
4. The solution was allowed to gently mix for approximately 10 minutes. The solution pH, ORP and temperature were recorded at the end of the reaction time.
5. Solids were allowed to settle for approximately 2 minutes after the end of the reaction time.

6. Samples of treated solution were filtered at $0.45\,\mu$m and submitted for laboratory analysis.

Key findings from the small- and large-batch tests included the following:

- Copper removal was nearly in direct proportion to the sulfide dosage, with essentially 100% copper removal occurring at a sulfide dosage of about 110% to 115% of the stoichiometric demand. Copper removal as a function of sulfide dosage is summarized in Fig. 2 for the small- and large-batch tests.
- Near-complete silver removal was affected at all sulfide dosages. It appears silver is preferentially removed over copper.
- Thiocyanate formation as a result of sulfide reacting with cyanide did not appear to be significant. For most tests, an average of about 2 mg/L thiocyanate was formed, but this level of thiocyanate formation would appear to be within analytical error. Formation of thiocyanate is an undesirable side reaction, since it results in the loss of cyanide.
- Sulfuric acid dosages required to adjust the solution pH to approximately 4.50 ranged from about 0.9 to 2.2 g/L H_2SO_4, with the samples containing higher levels of copper exhibiting the highest levels of sulfuric acid consumption. A higher level of sulfuric acid consumption for solutions containing higher levels of copper is expected, since these samples will normally have higher cyanide levels and sulfuric acid consumption is typically proportional to the cyanide level.

Continuous throughput test. A continuous throughput SART test was conducted with about 90 L of bulk sample Y4C-300. The continuous throughput system was operated for approximately 6.5 hours with sulfide addition, sulfuric acid addition, solids thickening and solids recycle steps (see Fig.
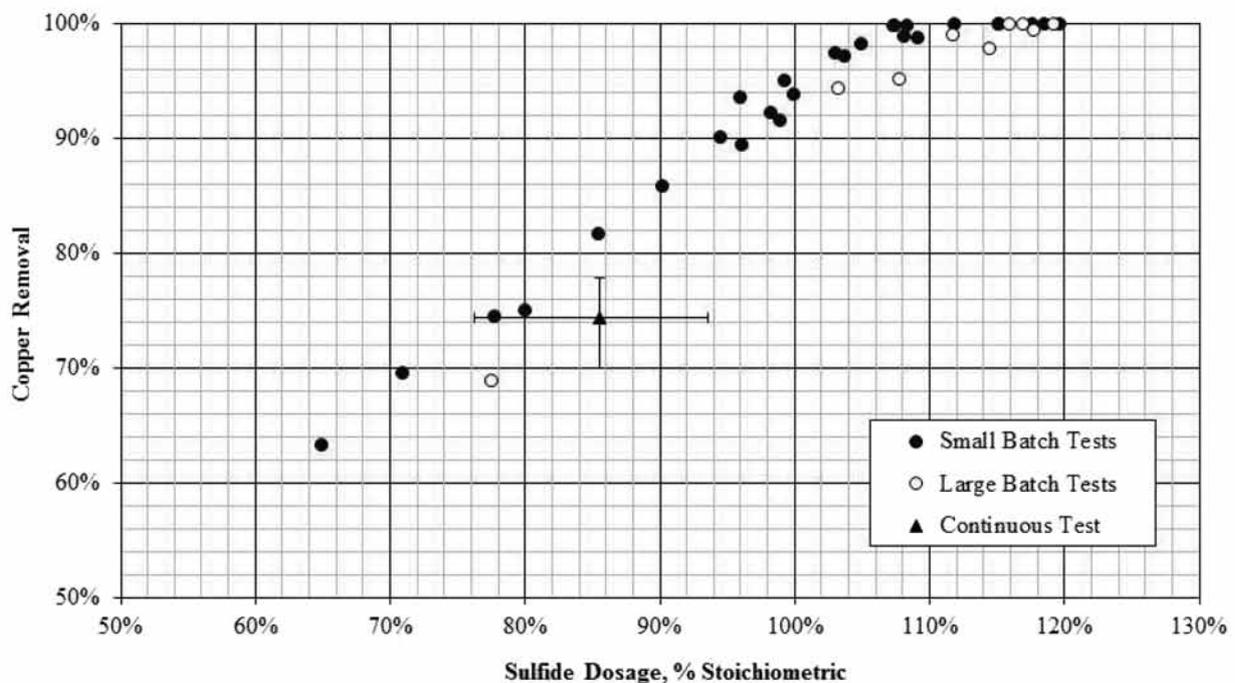
Figure 2 — Copper removal as a function of sulfide dosage.

1). Flocculant was not utilized in the solids thickening step in order to avoid altering the character of the solids prior to conducting solid-liquid separation testwork. Neutralization of the treated sample was conducted in a separate large batch test rather than with the continuous throughput system. Batch neutralization was selected due to the relatively small volume of leach solution available for testing and the inadequate period of operating time available to generate a useful quantity of gypsum precipitate.

The purpose of conducting the continuous throughput test was to determine if treatment performance under dynamic conditions (i.e., continuous flow) was similar to that observed under static conditions (i.e., batch testing). In addition, continuous throughput testing allowed the recirculation of thickener underflow solids to take place for a period of time, thereby generating solids thought to more closely represent solids that would be generated in the actual operation.

For the continuous throughput test, copper removal was generally consistent with that observed in the small- and large-batch tests. However, the sulfide dosage averaged only about 86% of the stoichiometric demand for the test, with the underdosage being the result of a higher than expected copper levels in the feed solution. A copper level of about 310 mg/L was calculated for the feed solution; however, the actual analyzed copper level in feed solution was about 460 mg/L. The differences in the calculated and actual copper levels was due to erroneous solution assays reported for individual samples blended to yield year-by-year leach solution composites. For this reason, copper removal during the testwork averaged only about 74%. However, this level of copper removal is consistent with batch test data shown in Fig. 2.

Sulfuric acid consumption for the continuous throughput test was approximately 10% higher than that observed in the small and large batch tests.

To estimate the dosage of lime required to neutralize treated solution, a portion of thickener overflow solution generated during the continuous throughput test was neutralized with calcium hydroxide (hydrated lime). Neutralization testwork was carried out by adding weighed increments of hydrated lime into the sample of solution being continuously mixed. After each incremental dosage of hydrated lime, the solution pH was recorded once stabilized. A hydrated lime dosage of approximately 0.9 g/L $Ca(OH)_2$ was required to adjust the solution pH from about 4.8 to 10.5. The solution was only mildly buffered in the pH range of about 4.8 to 8.5, with a relatively small dosage of hydrated lime causing a large change in pH in this range.

Precipitate assays. Filtered solids generated from the

large-batch tests were dried and submitted for elemental assays. Results from the assays are summarized in Table 2. As expected, the dominant element in the assay was copper, at approximately 68% to 74% by weight in the precipitates. Conversion of the copper assays to equivalents as Cu_2S suggest the precipitates consisted of approximately 85% to 93% by weight Cu_2S. Other elements present in the precipitate at appreciable levels included calcium (likely in the form of gypsum), iron, molybdenum, sodium and zinc. Concentrations of gold ranged from about 7 to 36 ppm in the precipitate, with higher levels of gold appearing to correspond to higher levels of copper precipitated from solution.

Solid-liquid separation testwork. Solid-liquid separation testwork was conducted using a slurry sample (thickener feed) generated during the continuous throughput testwork. Testwork was conducted at an acidic pH to mimic conditions that will be encountered during actual operation.

Flocculant screening tests were conducted with thickener feed slurry at pH 4.5, a temperature of 20° C and an initial slurry solids concentration of 1.1% by weight. Results suggest a flocculant dosage of approximately 40 to 50 g/t of solids will be required to produce good solids settling rates and reasonable supernatant clarity. The recommended flocculant was Hychem AF 305, a medium-to-high molecular weight 20% charge density anionic polyacrylamide.

Static thickening tests were conducted to determine the appropriate size of a conventional thickener for removing precipitated sulfide solids from treated solution. Tests were conducted at pH 4.5, a temperature of 20° C and feed solids concentrations ranging from 0.25% to 1.0% by weight with 40 to 60 g/t dosage of Hychem AF 305 flocculant. Results indicate that thickener feed solids should range from about 0.5% to 1.0% by weight with 40 to 50 g/t dosage of Hychem AF 305 flocculant. For the full-scale plant, maintenance of 0.5% to 1.0% solids in the thickener feed slurry will require recirculation of thickener underflow slurry into untreated solution (standard practice for a SART plant). The thickener underflow slurry density was found to range from about 12% to 16% solids by weight. The thickener sizing criterion (conventional thickener) was determined to be 2.5 to 5.0 m^2 of settling area per t per day of feed solids (m^2/t/day).

Recessed-plate pressure filtration tests were conducted using samples of neutralized thickener underflow slurry at pH 11.0 and 2.8% to 15.0% solids by weight. Filter cakes containing 60% moisture were produced following application of approximately two pore volumes of wash water. Filter cake bulk density is expected to be about 532 kg/m^3 on a dry basis and about 1,330 kg/m^3 on a wet basis. To form a 30-mm thick filter cake, a specific filtration rate of 2.35 m^3/t/day (25.9 kg/m^2/hour) was determined.

Laboratory testwork summary. The following were concluded from the laboratory testwork:

1. A reaction pH of approximately 4.0 to 5.0 was required to maximize the precipitation of copper.
2. An increase in the sulfide dosage resulted in increasing levels of copper removal, up to the point where near-complete copper removal was reached. Essentially complete copper removal occurred at a sulfide dosage of about 110% to 115% of the stoichiometric demand (based on copper, silver and zinc levels in untreated solution).
3. Near-complete removal of silver from pregnant leach

Table 2 — Summary of precipitate assays.		
Sample Code	**Copper (wt%)**	**Gold (ppm)**
Y3/7-300	70.8%	10.7
Y4-300	72.2%	34.4
Y4C-300	74.4%	7.0
Y4-500	72.4%	27.3
Y4-750	68.2%	36.2
Y5-300	72.8%	26.3
Y6-300	73.8%	25.2
Y8-300	73.2%	23.3
Y9-300	73.4%	33.1

solution was affected at all sulfide dosages. It appears silver is preferentially removed over both copper and zinc.

4. Assays of precipitated solids suggest a small portion of gold was removed from pregnant leach solution as a result of copper sulfide precipitation. Gold removed from solution following sulfide precipitation ranged from about 0.2% to 1.7% of the untreated leach solution gold concentration, equivalent to a reduction in the gold concentration of about 0.002 mg/L to 0.041 mg/L. It appears a higher level of copper removal from solution also resulted in a higher level of gold removal from solution.

5. Thiocyanate formation as a result of sulfide addition did not appear to be significant, but analytical data were variable and did not yield a firm conclusion.

6. The sulfuric acid dosage required to adjust pregnant leach solution to pH 4.5 was approximately 0.90 to 2.25 g/L H_2SO_4. Leach solution samples containing higher levels of copper exhibited the highest levels of sulfuric acid consumption.

7. For the sulfide thickener, feed solids concentration was recommended to be about 0.5% to 1.0% by weight with a flocculant dosage of about 40 to 50 g/t of Hychem AF 305.

8. Sulfide thickener underflow slurry density was found to range from about 12% to 16% solids by weight. The thickener sizing criterion (conventional thickener) was determined to be 2.5 to 5.0 m^2/t/day.

9. Neutralization of sulfide thickener underflow slurry (2.1% solids) from pH 4.5 to 11.0 required approximately 0.82 g/L of hydrated lime ($Ca(OH)_2$). A similar lime consumption is expected for slurry containing 12% to 16% solids since it is predominantly the solution being neutralized rather than the solids.

10. Filtered sulfide solids are expected to contain about 60% moisture following application of approximately two pore volumes of wash water and completion of an air blow. Filter cake bulk density is expected to be about 532 kg/m^3 on a dry basis. To form a 30-mm thick filter cake, a specific filtration rate of 2.35 m^3/t/day (25.9 kg/m^2/hour) was determined.

11. The dominant element in precipitated solids was copper at approximately 67% to 74% by weight. Conversion of the copper assays to equivalents as Cu_2S suggest the precipitates consisted of approximately 85% to 93% by weight Cu_2S. Other elements present in the precipitate at appreciable levels included calcium (likely in the form of gypsum), iron, molybdenum, sodium and zinc.

12. Approximately 0.35 to 0.90 g/L of $Ca(OH)_2$ was required to neutralize acidic thickener overflow solution to pH 10.5.

13. The amount of neutralized gypsum solids generated during laboratory testwork was insufficient to permit solid-liquid separation testwork to be conducted for the gypsum thickener.

Heap leach modeling

A computer simulation model of the heap leach facility being operated the Çöpler Gold Mine was developed in 2009 and 2010. The facility was modeled using METSIM software and included the major processing steps planned for the operation. The primary objective of modeling the heap leach was to evaluate appropriate hydraulic sizing for the SART circuit with respect to controlled copper levels in pregnant solution.

Information was also generated to estimate pregnant leach solution flow and chemistry over the mine life and to estimate production rates of gold, silver, copper and zinc.

METSIM models a heap leach by dividing the heap into geometric sub-units called "blocks." Each block is used to store a defined volume of ore with specified metal content and recovery criteria and blocks are sequentially filled with ore according to their location in the heap and the ore stacking plan. A heap can be divided into a few hundred blocks or into several thousand blocks, depending on the overall heap size. Blocks are assembled adjacent one another and on top of one another such that the overall shape of the heap is captured. Multiple lifts are placed on top of one another (following the perimeter contour for each lift in the heap) in order to "build" the entire heap. For each time step used in the dynamic heap leach simulation, METSIM calculates the mass balance in every block that is filled with ore. Operating criteria are defined in model input for items such as ore moisture, head grades for gold, silver and copper (according to the mine plan), leach extraction curves and the leach cycle. The heap leach module is coupled with other unit operations in METSIM to simulate the overall metallurgical process according to the process flow diagram for the project.

For the Çöpler Gold Mine, the following unit operations were included in the model:

- Agglomeration (cement and lime addition) and pre-wetting of ore prior to placement on the leach pad.
- Stacking of ore on the leach pad according to the heap leach pad design, mine plan and stacking plan.
- Collection of pregnant leach solution and routing a portion of this solution to a SART plant for copper and silver recovery.
- Adsorption of gold in a carbon column circuit, with the feed consisting of pregnant leach solution plus solution treated in the SART plant.
- Fresh water and sodium cyanide make-up.
- Recycling of barren leach solution to the heap leach.

A wide variety of data can be extracted from the model once full convergence is reached, though for this project the data of primary interest are summarized in Fig. 3. This figure illustrates the effect of the SART plant hydraulic size on the resultant concentration of copper in leach solution fed to the carbon column circuit. In the model, the SART plant was placed into operation once the pregnant leach solution copper level reached 200 mg/L.

As shown in Fig. 3, in the absence of a SART plant, the leach solution copper concentration is estimated to increase gradually over the project life to a level of nearly 1,800 mg/L. As the size of the SART plant is increased, the leach solution copper concentration decreases. A SART plant size of about 200 to 300 m^3/hour generally limits the leach solution copper concentration to less than about 200 to 300 mg/L. From this work, it was determined the SART circuit should be sized for approximately 200 to 300 m^3/hour.

Concluding remarks

Based on analysis of ore samples for the Çöpler Gold Mine, Alacer determined there was a risk of excessively high copper levels developing in pregnant leach solution over the course of mine life. At present, the only large-scale commercial process to control copper levels in leach solution is via sulfide precipitation (SART process), which recovers copper in saleable form and regenerates cyanide for continued usage.
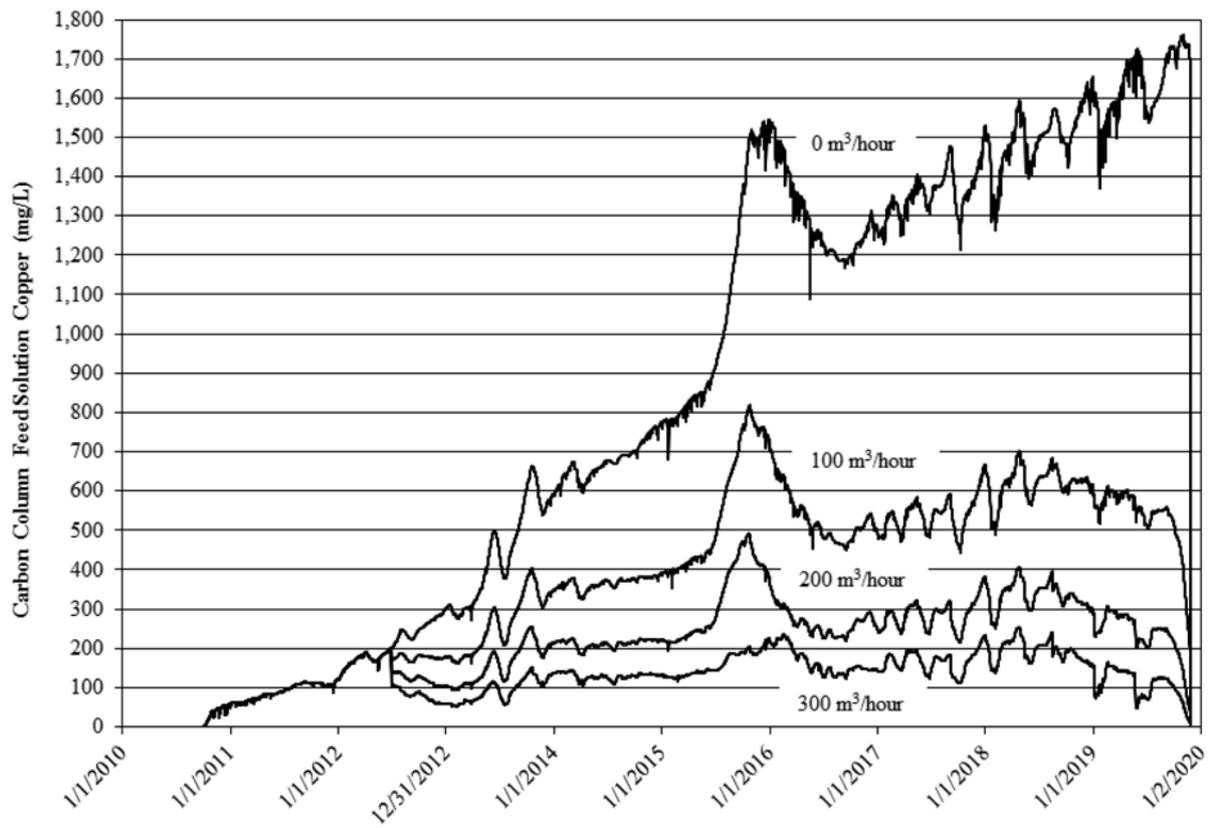
Figure 3 — SART circuit throughput versus leach solution copper concentration.

Alacer set out to evaluate the appropriate sizing basis for a SART plant, beginning with the mine plan and ending with modeling the entire metallurgical circuit. Associated work included the following:

- Development of a mine plan that included not only grades of gold and silver, but also grades of copper. Mine plan data included ultimate extractions (based on tested metal solubility in cyanide solutions) expected for gold, silver and copper for each ore type.

- Completion of metallurgical tests to evaluate performance of the SART process and to define preferred operating conditions.
- Integrated modeling of the heap leach circuit, SART circuit and carbon column circuit to evaluate the required hydraulic size of the SART circuit.

The above allowed Alacer to evaluate the entire metallurgical operation prior to design and construction and to consider various options at optimizing the operation.