COPPER PRECIPITATION AND CYANIDE RECOVERY PILOT TESTING FOR THE NEWMONT YANACOCHA PROJECT

Michael Botz, Elbow Creek Engineering, Billings, MT

Sevket Acar, Newmont Mining Corporation, Englewood, CO

Introduction

In 2007, Newmont Mining Corporation will begin construction of a milling and cyanidation leaching circuit for the Yanacocha site in Peru. Ore to be processed in the circuit contains a relatively high level of cyanide-soluble copper, and as a result, leach solutions are expected to contain elevated levels of copper and WAD cyanide. As the means of controlling copper levels in leach solution, a circuit will be installed to precipitate copper sulfide from barren solution using sodium hydrosulfide. In addition, a circuit will be installed to recover cyanide from barren solution, with recovered cyanide to be returned to the leaching circuit and treated solution to be utilized as makeup in existing heap leaching facilities. As needed to support design of the copper precipitation and cyanide recovery circuits, pilot testing was conducted in 2005 to determine preferred operating conditions and evaluate the performance of the processes. This paper presents results from the pilot testing where 99% copper reduction was achieved and 95% to 98% cyanide recovery was achieved.

Sample Preparation

Pilot testing was conducted in June 2005 in the USA with the primary purpose of characterizing the efficiency of copper precipitation and cyanide recovery processes for treatment of pregnant leach solution at Yanacocha. Leach solution used in the tests was generated from a relatively large bulk composite ore sample collected from the site.

For the pilot testing work, three large ore samples were collected from the Yanacocha site and blended to yield a 1,170 kg bulk composite sample. This sample was used as the source for generating leach solution for use in pilot testing the copper precipitation and cyanide recovery processes. The gold, silver and copper contents in this bulk ore sample are presented in Table 1.

Table 1. Bulk Ore Composite Sample

Assay	mg/kg
Au	2.45
Ag	43.1
Cu	2,080

The composite sample was ground to 76% passing 200 mesh (74 μ m) and leached in cyanide for 24-hours at 52% solids. To ensure a suitably high copper level in the pregnant solution, copper sulfate was added to the leach tank as a supplemental copper source to yield approximately 1,500 mg/L dissolved copper.

The chemistry of leach solution following 24 hours of leaching is presented in Table 2. Conditions for leaching were not ideal, therefore gold and silver extractions were lower than observed with laboratory bottle roll tests.¹ However, the objective of the test was not to evaluate gold and silver leach kinetics, but rather to generate a high-copper leach solution using representative samples of ore.

Table 2. Pregnant Leach Solution

Table 2.1 regnant Deach Solution		
Assay	mg/L	
Au	0.74	
Ag	3.11	
Cu	1,240	
CN-WAD	1,782	

Following 24 hours of leaching, the slurry was filtered and rinsed with fresh water (containing 10 mg/L free cyanide) at a ratio of 1.0 kg water per 1.0 kg of solids to simulate washing in a counter-current decantation (CCD) circuit at a 1:1 wash ratio. A total of approximately 2,080 liters of solution was generated for subsequent testing of the copper precipitation and cyanide recovery processes. The chemistry of this solution is presented in Table 3. As expected, the gold, copper and weak-acid-dissociable (WAD) cyanide levels following rinsing were

¹ Agitation of the leach tank was relatively poor.

approximately one-half of the levels in the pregnant leach solution (Table 2). However, the silver level slightly increased, though the reason for this discrepancy was not determined.

 Table 3. Pregnant Leach Solution following

 Filtration and Rinsing

Assay	mg/L
Au	0.41
Ag	3.25
Cu	653
CN-WAD	1,034

The leach solution characterized in Table 3 was used as the feed to the copper precipitation and cyanide recovery processes. An overall illustration of the sample preparation and treatment steps is provided on Figure 1.



Figure 1. Sample Preparation and Treatment Steps

Copper Precipitation Process

The process utilized in the pilot plant to precipitate copper from leach solution is commonly referred to as the Sulfidization, Acidification, Recycle and Thickening (SART) process. In this process, copper is precipitated from cyanidation solution as copper (I) sulfide following the addition of sodium sulfide (Na₂S) or sodium hydrosulfide (NaHS). As shown in Equation (1), the reaction requires one mole of sulfide per two moles of copper precipitated.

(1) $2Cu(CN)_3^{-2} + S^{-2} \rightarrow Cu_2S(s) + 6CN^{-1}$

Stoichiometric usage of sulfide is approximately 0.25 grams S^{-2} per gram of copper, 0.44 grams NaHS per gram of copper or 0.61 grams Na₂S per gram of copper. However, the actual sulfide dosage required for near-complete copper precipitation is normally in excess of 100% due to additional constituents that consume sulfide such as oxidants (e.g., dissolved oxygen) and other metals that react with sulfide.

The precipitation reaction takes place at a pH in the range of approximately 4.0 to 6.0 and results in nearly complete precipitation of copper. At this pH, free cyanide generated according to Equation (1) partitions to nearly 100% hydrogen cyanide, as shown in the following equilibrium relationship.

(2) $H^+ + CN^- \leftrightarrows HCN$

Due to the presence of hydrogen cyanide in the solution, care must be taken to avoid generation of dangerous levels of hydrogen cyanide gas. For pilot testing, all processing steps conducted at acidic pH were enclosed to the extent practical and the equipment was ventilated.

Equation (1) is written with respect to the $Cu(CN)_3^{-2}$ complex, but analogous reactions take place with the $Cu(CN)_2^{-}$ and $Cu(CN)_4^{-3}$ complexes. Of particular note in Equation (1) is the precipitation of copper that occurs simultaneously with the release of cyanide, thereby regenerating free cyanide from a previously complexed form.

In addition to precipitating copper, sulfide addition also results in the near-complete precipitation of silver, as shown in the following reaction.

(3) $2Ag(CN)_2^- + S^{-2} \rightarrow Ag_2S(s) + 4CN^-$

Because silver is precipitated along with copper, precipitate collected from the process can be of relatively high value. Other metals such as cadmium, molybdenum, nickel and zinc are also efficiently removed with this process to form their respective metal-sulfide precipitates.

Copper Precipitation Testing

As the first step in the process, sulfuric acid was added to the leach solution sample to yield a pH of approximately 5.0. Sodium hydrosulfide was then incrementally added until a slight sulfide residual was detected. Sulfide addition was not based on the calculated amount required to precipitate metals because of the unknown nature of sidereactions that would also consume sulfide. In addition, over-dosing of sulfide was deemed undesirable in order to avoid the presence of excess hydrogen sulfide in the solution. For this reason, sulfide was added incrementally with intermediate spot testing of the solution using the colorimetric cadmium nitrate method.

Following sulfide addition, sulfuric acid was added again to affect a final solution pH of approximately 4.3. Reagent dosages for the acidification and sulfide precipitation steps are summarized in Table 4.

Table 4. Reagent Dosages forSulfide Precipitation

Reagent	g/L
H_2SO_4	2.43
S ⁻²	0.55

The sulfide dosage of 0.55 g/L (as S^{-2}) relative to the solution copper concentration of 653 mg/L corresponds to a dosage of approximately 0.89 grams of sulfide per gram of copper, or approximately 340% of the stoichiometric requirement based on copper.

The chemistry of leach solution before and after sulfide precipitation is shown in Table 5. As indicated, copper precipitation was in excess of 99.1% and silver precipitation was in excess of 99.7%. A gold precipitation of about 10% was also indicated.

Of interest during the pilot testing was the amount of thiocyanate (SCN⁻) that would be generated through reaction of sulfide with cyanide in the leach solution. As indicated in Table 5, the thiocyanate concentration increased by about 63 mg/L, which is equivalent to the reaction of about 28 mg/L of cyanide with sulfide. Thiocyanate formation due to this reaction accounted for only a portion of the 10% WAD cyanide reduction observed, with the cause of the remainder of the reduction not determined.

Filtered solution from the sulfide precipitation step was neutralized to pH 10.0 using hydrated lime and then pumped through one carbon column containing approximately 12 kg of 6x16 mesh coconut shell granular activated carbon. The purpose of neutralizing the solution prior to carbon adsorption was to minimize the potential for HCN gas evolution in the adsorption system, which is anticipated to consist of open-top tanks in the full-scale facility. The chemistry of influent and effluent from the carbon column is presented in Table 6.

Assay	Before Sulfide Addition	After Sulfide Addition	
	mg/L		
Au	0.41	0.37	
Ag	3.25	< 0.01	
Cu	653	5.7	
CN-WAD	1,034	925	
SCN	305	368	

 Table 5. Solution Chemistry Before and After Sulfide Addition

Table 6. Solution Chemistry Before and
After Carbon Adsorption

Assay	Carbon Column Influent	Carbon Column Effluent	
	mg/L		
Au	0.37	0.07	
Ag	< 0.01	< 0.01	
Cu	5.7	8.7	
CN-WAD	925	793	
SCN	368	342	

As indicated in Table 6, the carbon column affected an 81% reduction in the gold level. Reductions in the WAD cyanide and thiocyanate levels of 14% and 7%, respectively, were also affected. The slight increase in the copper level was likely due to analytical variability.

Effluent from the carbon column was collected in a large tank and the pH re-adjusted to approximately 7.0 using about 1.25 g/L of sulfuric acid. The pH of 7.0 was selected since nearly all cyanide in solution at this point in the process was present as free cyanide, and at a pH of less than about 7.5, free cyanide is predominantly in the form of HCN, as shown on Figure 2. This solution was used as the feed to the cyanide recovery pilot plant.



Figure 2. HCN Distribution versus Solution pH

Precipitated Solids Characteristics

Approximately 3.7 kg of precipitate (dry basis) was collected by filtering solids from the leach solution after reaction with sulfide. This corresponds to a solids generation of approximately 1.78 g/L in the sulfide precipitation step. The composition of the precipitate is presented in Table 7, and as expected, the precipitate consisted primarily of copper. The analyses suggest the precipitate would consist of approximately 76.9% Cu₂S and 0.38% Ag₂S.

 Table 7. Sulfide Precipitate Analysis

Assav	mø/kø	wt%
Au	10.5	
Ag	3,275	0.33%
Cu		61.5%

Settled solids resulting from the sulfide precipitation step were further characterized with respect to filterability and settleability. Key results from this characterization are summarized below.

- A high molecular weight non-ionic flocculant at 0.25 mg/L was found to yield a good solids settling rate and good supernatant clarity.
- The density of settled solids in a gravity thickener would be approximately 3% to 5% solids by weight.
- The sizing basis for a thickener would be approximately 5 to 7 m²/tpd.

• Pressure filtration (recessed plate) would yield a cake containing about 65% moisture.

Cyanide Recovery Process

Solution generated from the sulfide precipitation and carbon adsorption processes was used as the feed to the cyanide recovery pilot plant. The chemistry of this solution is summarized in Table 8 following adjustment of the pH to 7.0.

Table 8. Cyande Recovery Teed Bolution		
Assay	mg/L	
Au	0.06	
Ag	< 0.01	
Cu	7.0	
CN-WAD	778	

Table 8. Cyanide Recovery Feed Solution

The process utilized for cyanide recovery is commonly referred to as the Acidification-Volatilization-Reabsorption (AVR) process. In this process, cyanide solution at an acidic pH is passed through a stripping tower where HCN gas is stripped from solution. The stripped HCN gas stream is then directed to an absorption tower where sodium hydroxide (NaOH) solution is used to re-absorb the HCN and generate a stream of recovered sodium cyanide (NaCN). The stripping and absorption reactions are shown below.

(4) $HCN(aq) \rightarrow HCN(g)$ <u>Stripping</u>

(5) $HCN(g) + NaOH \rightarrow NaCN + H_2O$ Absorption

A basic flow diagram of the cyanide recovery process is shown on Figure 3.

The consumption of NaOH indicated in Equation (5) for HCN absorption is about 1.48 kg NaOH per kg HCN absorbed. Due to the short-term operation of the AVR pilot plant the actual consumption of NaOH in the absorption tower could not be quantified. However, in practice it has been found the consumption is commonly about 10% above the stoichiometric, or about 1.63 kg per kg of HCN absorbed. Elevated levels of dissolved carbon dioxide and/or hydrogen sulfide would increase the consumption of NaOH due to their stripping and absorption in the AVR system.



Figure 3. Cyanide Recovery Flow Diagram

Cyanide Recovery Testing

For the pilot plant, a small continuous-throughput AVR pilot plant was utilized to process the 2,080 liters of leach solution. During the testwork, the volumetric ratio of gas to liquid in the stripping tower and the height of packing in the stripping tower were varied to determine the effects on cyanide recovery. The temperature of solution treated in the AVR pilot plant averaged approximately 17°C.

The effects of varying the gas to liquid ratio and the packing height in the stripping tower are summarized on Figure 4. Within the range of parameters tested in the cyanide recovery pilot plant, WAD cyanide recoveries of about 75% to 98% were affected. As indicated on Figure 4, a higher gas to liquid ratio and/or a larger packing height is required to increase the cyanide recovery. To obtain 95% or higher cyanide recovery, a gas to liquid ratio in the range of about 600:1 to 800:1 was required with a packing height of about 5.2 to 7.0 meters. Data from the cyanide recovery pilot testing are also presented in Table 9.

Samples of effluent from the AVR pilot plant were neutralized with hydrated lime, and it was determined that approximately 0.05 g/L hydrated lime was required to neutralize the pH from 7.0 to 10.5.

Summary

In summary, copper precipitation and cyanide recovery pilot testing indicated the following with respect to the Yanacocha leach solution.

- Sulfide addition to the Yanacocha pregnant leach solution yielded greater than 99% removals of both copper and silver and approximately 10% removal of gold. Sulfide addition to the point of a slight excess required a significant stoichiometric excess, suggesting that testing of the process is required for each application to gauge reagent consumptions.
- Precipitated solids resulting from sulfide addition were estimated to gravity settle to a density of approximately 3% to 5% solids by weight with a small flocculant dosage. Filtration was estimated to yield a filter cake containing approximately 65% moisture by weight.
- Precipitated solids resulting from sulfide addition contained approximately 61.5% copper and 0.33% silver by weight, indicating a high commercial value relative to its silver content.
- A minor amount of cyanide was converted to thiocyanate as a result of sulfide addition.
- Under optimized operating conditions, 95% to 98% WAD cyanide recovery was affected, yielding an effluent containing less than 50 mg/L WAD cyanide.



Figure 4. Cyanide Recovery Test Results

Strippin	g Tower		WAD Cyanide	
Packing Height	Gas to Liquid	Influent	Effluent	Percent
(m)	Katio	(mg/L)	(mg/L)	Recovery
3.66	425	688	123	83.1%
3.66	599	690	72	89.5%
3.66	847	685	39	94.1%
3.66	1,081	682	20	97.2%
5.18	357	699	175	75.1%
5.18	447	687	110	84.2%
5.18	521	702	80	88.9%
5.18	625	697	56	92.4%
5.18	762	710	28	96.2%
5.18	904	704	15	98.0%
7.01	378	688	93	86.7%
7.01	446	711	55	92.6%
7.01	598	688	34	95.2%
7.01	688	688	24	96.6%
7.01	805	698	17	97.7%
7.01	839	692	16	97.9%
7.01	844	685	14	98.0%
7.01	990	704	18	97.1%