

OPERATIONAL PRACTICES TO REDUCE COPPER AND OTHER METALS LOADING ONTO ACTIVATED CARBON IN HEAP LEACH CIC CIRCUITS

B. Cousins, Newmont Mining Corp., Carlin, NV
T. Seal, Everclear Solutions, Inc., Emeryville, CA
A. C. Caraballo, Univ. of Nebraska-Lincoln, Lincoln, NE

INTRODUCTION

Copper, nickel, zinc and other “penalty” metals are found with gold together in nature, and have a similar chemical affinity for cyanide used in leaching operations⁴. As a result, solutions that come from the heap leach pads contain a significant concentration of penalty metals along with the desired gold. In solution, gold and cyanide form the complex $Au(CN)_2^-$ that is readily adsorbed onto activated carbon. Penalty metals as individual metal ions also load onto activated carbon and, depending on the concentration of cyanide and the pH of the solution, can form various cyanide complexes. Some of these complexes can also load onto carbon while some are significantly inhibited from loading. Copper, for example, can form the dicyanide complex $Cu(CN)_2^-$, the tricyanide complex $Cu(CN)_3^{2-}$, and the tetracyanide complex $Cu(CN)_4^{3-}$. At a low pH and a low concentration of cyanide, the dicyanide complex predominates. At a higher pH and a higher concentration of cyanide, the tetracyanide complex predominates. Without excess cyanide, however, individual copper ions can remain present.

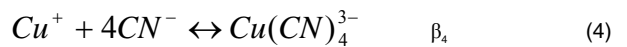
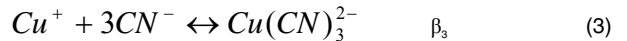
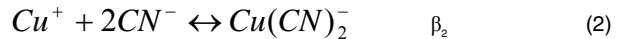
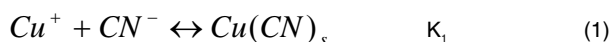
Activated carbon is used in gold extraction because it is highly selective for gold and less so for other metals, such as copper⁵. However, copper has the ability to adsorb (“load”) onto activated carbon and block the adsorption of gold when it is in the dicyanide form and in a high enough concentration. When copper is in the tetracyanide form, copper loading is significantly inhibited, allowing for the maximum gold recovery. In order to ensure the tetracyanide complex is formed, a combination of both available cyanide and elevated pH must be present.

In the South Area of Newmont Mining Corporation’s Gold Quarry mine in Carlin, Nevada, copper and nickel loading becomes a problem when certain acid generating zones of the heap are leached. Copper, nickel, zinc and other penalty metals become leachable and the lower pH uses up more of the cyanide and creates carbon loading conditions for the metals. This decreases the carbon’s ability to extract the gold from solution, decreasing the recovery and increasing the concentration of gold in the barren solution that leaves the carbon columns.

In this study, operational data from March through to May of 2007 is presented to show how Newmont developed a quick fix to lower pH and elevated metal concentrations that were causing low gold loadings on activated carbon at their South Area Leach (SAL) heap leach operations. Laboratory tested were also conducted to examine the chemical kinetics of metal loading and the individual effects of increased cyanide concentrations.

THEORY

Copper I ions form four different complexes with cyanide in solution: the monocyano species $CuCN$, the dicyano species $Cu(CN)_2^-$, the tricyano species $Cu(CN)_3^{2-}$, and the tetracyano species $Cu(CN)_4^{3-}$. The species are formed from the following reactions:



where K_i equals $10^{19.50}$, β_2 equals $10^{24.03}$, β_3 equals $10^{28.65}$, and β_4 equals $10^{30.35}$. Along with these complexing reactions, hydrogen cyanide and water also dissociate in solution, as per the following reactions:



where K_H has a value of $10^{9.24}$ and K_W has a 10^{14} value². These six chemical equations compete with each other, with domination of one over the others dependent on the CN^- and H^+ concentrations.

Each complex also has different properties when it comes to its loading behavior on activated carbon. The dicyano copper complex and the monocyano copper complex have an affinity for adsorption onto activated carbon that is greater than the affinity of gold cyanide for adsorption. They also have a lower solubility in water, which enhances adsorption. The tricyano copper complex and the tetracyano copper complex are water soluble and have an affinity for loading adsorption on activated carbon that is less than the affinity of gold cyanide for loading adsorption¹.

There are three prime reasons for this phenomenon. First, the extra cyanides mask the metal ion more, which blocks the main adsorption characteristic of the complex. Second, the complexes are also larger, making it harder to physically fit into the active sites on the carbon. This helps make the latter two complexes kinetically inhibited from adsorption, freeing carbon active site to load with gold cyanide complexes.

Third, it is also important to consider the expressions of the mass and charge balance. These balances describe all the overall concentration of copper and cyanide in solution, as well as marking overall charges of the ions in solution⁴. This is important because significantly changing the charge from positive/neutral to more negative is another reason for activated carbon to reject adsorbing the higher cyanide complexes.

The speciation of copper and other penalty metal cyanide complexes in solution is dependent on the pH. At lower pH values, increased hydrogen ions (H^+) can out-compete metals for cyanide ions. Lower free cyanide in the system leads to the lower cyanide species of copper cyanide predominating, with a noticeable concentration of the free metal, monocyano and dicyano species of copper cyanide. At higher pH values, hydrogen ions are significantly reduced, reducing the kinetics of HCN formation. More free cyanide remains in the system, allowing for more complexing. With this higher amount of cyanide in the system, the tetracyano species of copper cyanide predominates, also with a noticeable concentration of the tricyano species of copper cyanide. Higher copper concentrations, however, require more

cyanide to actually get to the tetracyanide complex. It also follows that high cyanide concentrations at low pH will tend to push some of the copper to tetracyanide. Only two of the four cyanide species exist in significant concentrations at a given pH value⁵. Figure 1 graphs the copper cyanide complexes versus cyanide concentration. Note the large amount of cyanide needed to push copper to tetracyanide.

Nickel has its own pH levels that create loading or inhibition to carbon loading. Nickel has a higher solubility than copper and other penalty metals at higher pH, causing it to be a little more problematic in heap leach operations. However, ores produced at the Carlin operations of Newmont do not have significant nickel concentrations, minimizing the effects.

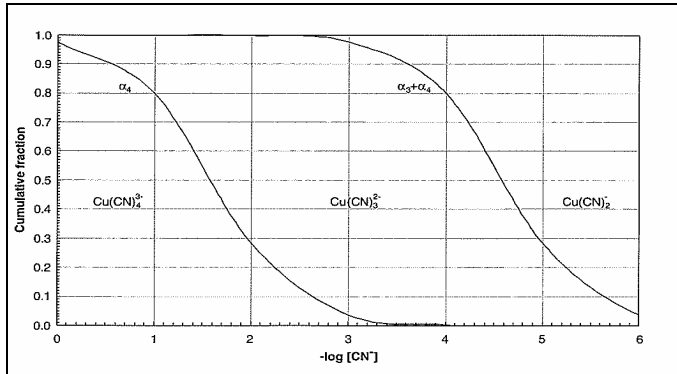


Figure 1. Logarithmic Diagram for the Cumulative Distribution of Cuprous Ion-Cyanide Species as a Function of Free Cyanide Ion Concentration.

OPERATIONAL DATA

The CIC circuit at South Area Leach (SAL) is illustrated in Figure 2. Three trains of six columns each are fed pregnant solution from the pond through a pump. The flow cascades down through the columns via gravity, fluidizing approximately 7000 lbs of carbon in each column. Each column is 118 inches tall and 126 inches in diameter. Flow rate is maximized at approximately 4400 gallons per minute per train. In April of 2007, a three column train with columns 78 inches tall and 134.5 inches in diameter was commissioned, increasing the total flow capacity by 2000 gallons per minute. Cyanide is generally added in the barren sump prior to being pumped back out to the leach pads. The 28%-32% NaCN solution also contains NaOH used to maintain a high pH and it is added to barren sump to produce 0.2 to 0.25 lbs per ton of solution concentration. The pH jumps from 8.5 to 9.2 with the addition.



Figure 2. Carbon Columns at SAL, Newmont Mining, Carlin Nevada.

Centering on the top columns of the three carbon CIC trains at SAL, data was collected on how much of the gold was adsorbed, copper and nickel levels, and pH and free CN concentrations over a

period of three months. In late April and early May of 2007, severe Au loading problems occurred, with May 4 being the worst. Figure 3 is a graph of the copper and nickel concentration in the pregnant solution. It shows elevated copper and nickel concentrations, peaking around April 17 and then slowly declining. It was during March that acidic side hills were being leached, producing copper and nickel concentrations well above what was considered normal. The pH of these leach solutions were generally acidic and below 4, so they were neutralized with other solutions to bring the pH up to an acceptable range.

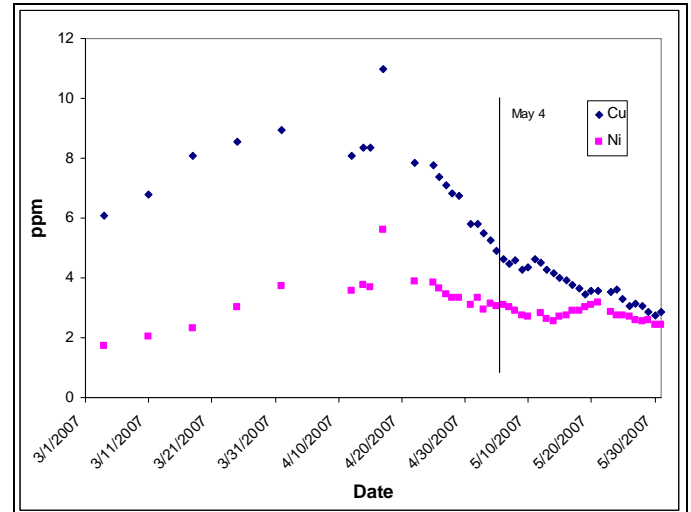


Figure 3. Copper and Nickel Concentrations from March 2007 through to May 2007.

The free cyanide concentrations in the pregnant solution were high as well, being able to counteract the copper and nickel concentrations somewhat until some time in late April. During this time, gold recovery in the top columns was not performing well, but was not seriously affecting total recovery over the length of the train of CIC columns until the last few days of April, where the serious decline in recovery in the top columns coincided with enough of a reduction in free cyanide to tip the balance of gold loading over penalty metals towards the penalty metals. After May 4, with the cyanide addition moved to the top of the columns, free cyanide and pH were adjusted back into a favorable zone to keep penalty metals from loading. Figure 4 shows the declining cyanide concentration in the pregnant solution as well as the pH and cyanide concentration in the barren solution after the addition of cyanide, which would be reasonably equivalent to what the pregnant solution would become with the cyanide addition location changed to the top of the CIC column trains.

Figure 5 and Figure 6 match up the gold loading and gold recovery with the events around May 4, with a significant drop in recovery and gold loading onto carbon during that time.

On May 5, the addition location of 0.25 lbs per solution ton of cyanide was moved from the barren sump to the top of the CIC columns, bringing with it both extra cyanide and a pH boost to over 9. The dramatic turnaround is also seen in Figures 4 and 5 after the May 4 line. Gold recovery jumped back up into the range it was in at the beginning of March while gold loading in the top columns recovered as well. The rate of increase was tempered by penalty metal concentrations on the carbon in lower CIC columns as they were advanced upward through the trains. The dramatic drop in top column loading was matched by a nearly as dramatic increase once the cyanide addition location was changed.

The cyanide addition to the top of the CIC trains was continued until June of 2008, at which time with the copper and nickel levels sinking to under 4 ppm combined, the cyanide addition location was put back into the barren sump. Pregnant solution pH during the test time and through to October 2008 did not significantly change, averaging around 8.5.

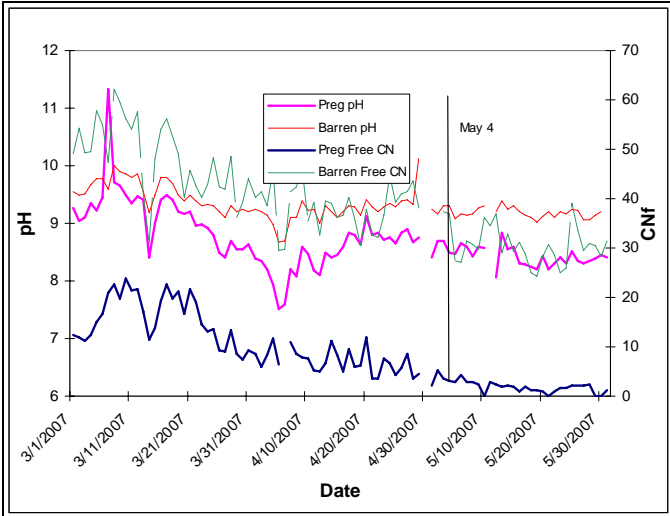


Figure 4. pH and Cyanide Concentrations in Pregnant and Barren Solutions from March to May 2007.

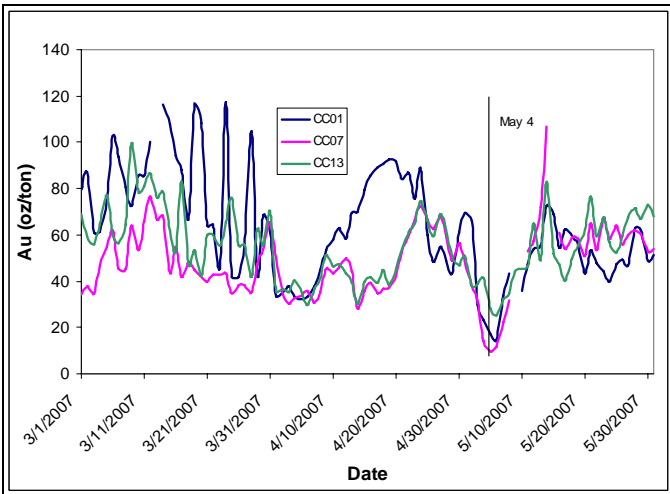


Figure 5. Gold Loading on Carbon, First Columns from March to May, 2007.

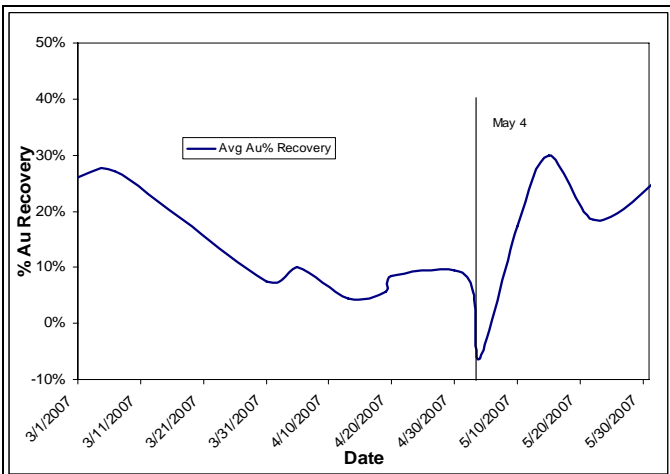


Figure 6. Average Gold Recovery at Top of CIC Trains from March through May, 2007.

LABORATORY STUDIES

A laboratory testing program was undertaken to see the effects of increasing cyanide complexing without pH adjustment at a pH of

approximately 8. Time limitations did not allow the testing of pH variations. The end result was to see the need for both pH and cyanide increases to effectively inhibit copper and nickel loading onto activated carbon as suggested in the plant data.

Experimental Design

The program involved using 150g of new activated carbon added to five lab carbon columns. Five 20 L plastic buckets were filled with pregnant solution from SAL daily. 5 pumps were used to move pregnant solution from each bucket through its corresponding carbon column, pumping at 12 mL/min to mimic SAL operations. A bucket supplies 17.3 liters of solution through the column in a 24 hour period.

Nickel and copper sulfate were used to prepare spike solutions for the first run while Cu(CN)₂ and Ni(CN)₂ salts were used for the second run to ensure enough cyanide was available to complex all the copper and nickel. In bucket control, there was no added nickel and copper. In buckets 1-4, increasing quantities of the nickel and copper spike solutions were added, as shown in Table 1 below.

Table 1. Amount of Cu/Ni spike Solution Added to Buckets with Approximate Final Concentrations after ppt.

Bucket	Spike Soln (mL)	SO4 ppm		CN4 ppm	
		Cu	Ni	Cu	Ni
Control	0	2.74	1.15	2.83	1.05
1	40	5.12	2.98	6.67	2.73
2	80	5.04	3.66	10.63	4.39
3	160	6.06	6.18	20.00	8.29
4	320	7.00	11.10	37.51	15.58

For 24 hours, nickel, copper, and gold loaded onto the activated carbon. A sample of carbon was then removed from each column and analyzed by ICP to determine each metal loading. Fresh pregnant solution was prepared with the spike solution and run through the remaining carbon for another 24 hours. This was repeated for 4 days. Figure 7 is a diagram of the testing apparatus

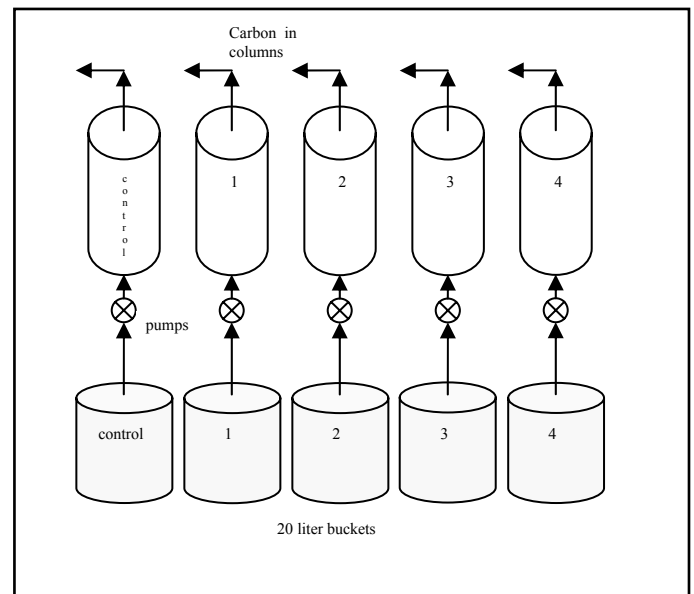


Figure 7. Design of experimental carbon column/bucket system used for testing effects of copper and nickel loading as metals and as tetracyanide complexes at low pHs.

Experimental Data

The results from the testing program show that without a pH increase, having enough cyanide to complex copper and nickel to tetracyanide does not inhibit copper and nickel from loading.

The first set of tests with a spike solution made from copper and nickel sulfate proved problematic. As suspected, copper precipitated

as a hydroxide out of the solution at the pH of approximately 8.4. Nickel precipitated a little as well, but nickel hydroxide has a much higher solubility so mostly only the copper concentration was seriously affected. When copper and nickel are added as tetracyanide complexes, the metal solubilities are much higher, producing higher metal content for the tests. Table 1 lists the copper and nickel concentrations as they really were during this part of the testing phase.

Sulfate Spike Solutions

Copper, nickel and gold loading onto carbon with sulfate spike solutions are listed in Table 2. Note that the gold loading was not overly affected by higher copper and nickel levels, but this is likely due to the high activity of the carbon. The pregnant solutions during the testing period were approximately 0.0054 oz/ton of gold with a pH of 8.4, which converts to 0.169 ppm. The 30 to 180 fold increase in copper/nickel combined concentrations of the test solutions also show that even if gold still had a kinetics advantage for loading, it would have been compromised by the significantly higher penalty metal concentrations.

Table 2. Carbon Loading from Sulfate Spike Solutions.

	Day	Au (oz/ton)	Cu (ppm)	Ni (ppm)
Control	1	0.79	204	88
Column 1	1	0.57	374	208
Column 2	1	0.22	216	169
Column 3	1	0.45	341	321
Column 4	1	0.88	700	503
Control	2	1.43	526	253
Column 1	2	1.40	682	433
Column 2	2	1.47	861	519
Column 3	2	1.58	1205	901
Column 4	2	0	1572	888
Control	3	2.16	647	326
Column 1	3	1.95	1566	963
Column 2	3	1.94	1299	907
Column 3	3	2.64	1563	994
Column 4	3	2.39	1922	1189
Control	4	3.23	936	435
Column 1	4	3.28	1970	1128
Column 2	4	3.08	1905	1252
Column 3	4	2.87	2235	1336
Column 4	4	3.57	3460	1437

Table 3. Carbon Loading from Tetracyanide Spike Solutions.

	Day	Au (oz/ton)	Cu (ppm)	Ni (ppm)
Control	1	0.66	121	43
Column 1	1	0.83	616	278
Column 2	1	0.64	818	384
Column 3	1	0.16	897	461
Column 4	1	0.44	1913	1131
Control	2	1.42	405	179
Column 1	2	1.22	852	450
Column 2	2	1.23	1582	912
Column 3	2	0.87	1726	1033
Column 4	2	1.31	2616	2050
Control	3	1.35	811	357
Column 1	3	3.02	1637	804
Column 2	3	1.55	2341	1348
Column 3	3	2.23	2131	1279
Column 4	3	3.54	3382	2894

The data for the sulfate spike solutions tests clearly show that increased copper and nickel concentrations in a pregnant solution lead to higher copper and nickel loadings on the carbon as expected. This

data is the baseline for which the tests using tetracyanide copper and nickel salts will be compared to. Determining how much copper and nickel loads given equivalent metal concentrations of the two spiked solutions is the goal.

Tetracyanide Spiked Solutions

The tetracyanide copper and nickel salts produced solutions with considerably higher copper and nickel concentrations than the sulfate spiked solutions. These complexes are much more resistant to the formation of hydroxides that can precipitate out. And with the tetracyanides, the amount of cyanide required for the non-loading metal complexes to form is there, so the pH can be studied for its potential to strip some of the cyanides off the metals, creating dicyanide loading complexes. The test was run for 3 days.

Any comparisons between the sulfate and tetracyanide data must be made after standardizing the copper and nickel metal contents of the two tests. The tetracyanide solutions produced higher metal solution contents than the sulfate solutions due to less hydroxide precipitation. Therefore, columns 1 through 4 for the two different spiked solutions do not line up directly.

Table 4. Comparisons of Sulfate and Tetracyanide data Compared with Similar Copper Concentrations in ppm.

Column	Day	CuSO4 Soln	carbon	CuCN4 soln	carbon
Control	1	2.74	204	2.83	121
1				6.67	616
3		6.06	341		
4		7.00	700		
Control	2	2.74	526	2.83	405
1				6.67	852
3		6.06	1205		
4		7.00	1572		
Control	3	2.74	647	2.83	811
1				6.67	1637
3		6.06	1563		
4		7.00	1922		

Table 5. Comparisons of Sulfate and Tetracyanide Data Compared with Similar Nickel Concentrations in ppm.

	Day	NiSO4 soln	carbon	NiCN4 soln	carbon
Control	1	1.15	88	1.05	43
Column 1	1	2.98	208	2.73	278
Column 2	1	3.66	169	4.39	384
Column 3	1	6.18	321	8.29	461
Column 4	1	11.10	503	15.58	1131
Control	2	1.15	253	1.05	179
Column 1	2	2.98	433	2.73	450
Column 2	2	3.66	519	4.39	912
Column 3	2	6.18	901	8.29	1033
Column 4	2	11.10	888	15.58	2050
Control	3	1.15	326	1.05	357
Column 1	3	2.98	963	2.73	804
Column 2	3	3.66	907	4.39	1348
Column 3	3	6.18	994	8.29	1279
Column 4	3	11.10	1189	15.58	2894

From Table 1, it can be seen that columns 1 from the tetracyanide solutions line up more with columns 3 and 4 from the sulfate solutions for copper. Nickel lines up fairly well column to column. Table 4 lines up these loading comparisons for copper and Table 5 lines up the nickel loading comparisons.

With both copper and nickel, the presence of more cyanide does not appear to restrict loading onto carbon at a pH of 8.4. Comparable

copper concentrations gave similar loadings on the carbon and nickel for both sulfate and tetracyanide tests. Much higher free cyanide must be required to significantly suspend copper and nickel loading at a pH of 8.4.

CONCLUSIONS

Having enough free cyanide to complex all the copper and nickel to tetracyanide does not appear to be enough to form significant amounts of the tetracyanide complexes to inhibit copper and nickel loadings. At a pH of 8 to 8.5, the HCN/CN⁻ balance must still be consuming enough CN⁻ to strip the tetracyanide complexes of CN⁻ to obtain equilibrium. This is consistent with the data from operations that showed the decline in gold loading in the top columns as the pH and free cyanide started to lower in concentration during high copper and nickel concentrations in the pregnant solution. A combination of high pH and cyanide concentrations is the best method to suppress penalty metal loading.

ACKNOWLEDGMENTS

The authors would like to thank Newmont Mining Company for their support of this work and Susan Steblay of the Colorado School of Mines for her invaluable work in the laboratory studies.

REFERENCES

1. Bachiller, D., Torre, M., Rendueles, M., & Díaz, M. (2004). "Cyanide recovery by ion exchange from gold ore waste effluents containing copper." *Minerals Engineering*, 17, 767-774.
2. Lee, J.S., Deorkar, N.V., & Tavlarides, L.L. (1998). "Adsorption of copper cyanide on chemically active adsorbents", *Industrial & Engineering Chemical Research*, 37(7), 2812-2820.
3. Marsden, J.O., & House, C.I. (2006). *The chemistry of gold extraction*. Littleton: Society of Mining, Metallurgy, and Exploration, Inc.
4. Torre, M., Bachiller, D., & et al. (2006). "Cyanide recovery from gold extraction process waste effluents by ion exchange, I. Equilibrium and kinetics", *Solvent Extraction and Ion Exchange*, 24, 99-117.
5. Lemos Flavio, Dutra Achilles "Copper electrowinning from gold plant waste", www.cetem.gov.br/publicacao/CTs/CT2006-024-00.pdf.