

Thermophilic Bioheap Leaching of Chalcopyrite Concentrates

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ABSTRACT

The extraction of copper from chalcopyrite has for centuries been limited to pyrometallurgical methods. Smelting of chalcopyrite is an efficient process but costly both in terms of capital investment, operating costs and environmental compliance. Biological extraction appeared as an appealing alternative. Unfortunately, traditional mesophilic biological extraction methods have met with little success. The chalcopyrite quickly becomes passivated and unacceptable copper extractions are achieved. It was not until the adoption of thermophilic systems that the biological leaching of chalcopyrite became a reality. Several questions remain as to the applicability of the thermophilic system for chalcopyrite; can the system operate auto-thermally; can high extraction rates be achieved; is the process sensitive to mineralogy or grade; and can the precious metals be recovered?

GeoBiotics, LLC has embarked on an extensive program to develop the GEOCOAT[®] bioleaching system to chalcopyrite ores. This program encompasses mathematical heap modeling, laboratory amenability and column tests, and large scale field trials. The GEOCOAT[®] process involves the coating of concentrates onto a suitable substrate, usually barren rock, then stacking the coated material in a conventional heap fashion. The heap is irrigated with acidic solutions containing iron and nutrients while low pressure ambient air is applied at the heap base.

To-date, copper extractions in excess of 97% have been achieved in approximately 140 days. Excellent gold extractions have been achieved from the biooxidation residue by cyanidation. Modeling indicates that obtaining thermophilic temperatures within the GEOCOAT[®] heap is not a problem. Development is continuing, focusing on the heap design parameters and additional copper concentrates including enargite. Plans are now underway for the first large scale field test in the fall of 2002. © 2002 SDU. All rights reserved.

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1. INTRODUCTION

Pyrometallurgy currently accounts for more than half of all non-ferrous metal production and nearly 95% of all metals produced (World Bureau of Metals Statistics, 1999), although iron and steel account for a large portion of this. There are approximately twenty important non-ferrous metals with a combined production of 100 million tonnes per year. Pyrometallurgy predates history, copper production by this method was first recorded in 4000 B.C. and still today just under 90% of the world's cathode copper is produced using this method (Eltringham, 1997).

Pyrometallurgy has clearly predominated in the past and still predominates today for the treatment of "clean" concentrates. The reasons for this are relatively straightforward; the process is fairly simple, reaction rates are faster and the precious metals are recovered easily. However, problems arise in the development of a metallurgically and environmentally acceptable method for treatment of complex sulphides. Not only is classical pyrometallurgy inflexible when it comes to treating complex sulphides efficiently, but also suffers from other inherent disadvantages such as:

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- High capital investments,
- High operating costs,
- Large volumes of waste gases containing SO₂ requiring fixation/purification,
- Dusts containing Pb, As, Sb, Cu, Zn, Hg, Bi, Se,
- Fugitive gases in the work environment,
- Large volumes of solid waste products.

It was not until the advent of hydrometallurgical methods in the 1950's that a viable alternative to pyrometallurgy was envisioned and not until the late 1970's when materials of construction advancements allowed for the first commercial pressure hydrometallurgy operation to commence (Parker, 1981). Bioleaching also began in the early 1950's although it could be debated that the use of bacteria was accidental as a result of the inadvertent colonization of endemic species surrounding copper dump leaches. It was not until much later that commercial dump leaching employing bacteria was begun, see Table 1 (Brierley, 2000).

Table 1
 Commercial Bioheap Leach Operations

Plant/Location	Size (tpd)	Operator	Ore Grade (% Cu)	Years in Operation
Lo Aguirre, Chile	16,000	Sociedad Minera Pudahuel	1.5	1980-Present
Mt. Leyshon, Australia	1,370	Normandy Poseidon	0.15	1992-1995
Cerro Colorado, Chile	16,000	Rio Algom	1.4	1993-Present
Girrilambone, Australia	2,000	Straits Resources	~3	1993-Present
Ivan, Chile	1,500	Glamis Gold	2.1	1994-Present
Quebrada Blanca, Chile	17,300	Cominco	1.3	1994-Present
Andacollo, Chile	16,000	Dayton Mining	1.0	1996-Present
Dos Amigos, Chile	3,000	Cemin	2.5	1996-Present
Cerro Verde, Peru	32,000	Cyprus-AMAX	0.7	1996-Present
Zaldivar, Chile	~20,000	Placer Dome	1.4	1998-Present
S&K Copper, Myanmar	15,000	Myanmar Government, Ivanhoe Copper	1.25	1998-Present

Dump leaching has several key advantages that make it useful for low grade oxide and secondary sulphide copper ores; the capital and operating costs are relatively low and the process is relatively simple. Unfortunately, dump leaching also suffers from two major drawbacks that prevent it from being economical for treating higher grade ores; long extraction times and moderate metal recoveries. Additionally, the principal primary copper sulphide, chalcopyrite, does not respond well to the mesophilic conditions found in most dump leaches.

Traditional mesophilic biological extraction methods for chalcopyrite extraction have met with little success. The chalcopyrite quickly becomes passivated and unacceptable copper extractions are achieved. It was not until the adoption of thermophilic systems that the biological leaching of chalcopyrite became a reality. There are several stirred tank processes currently being put forward for the biological extraction of copper from chalcopyrite including the BIOCOP[®] Process, the Mintec/Bactech Process and the HIOX[®] Process. Each of these systems uses elevated temperatures in the moderate or extreme thermophilic ranges to maintain bacterial populations suitable for chalcopyrite extraction. Although these processes have many advantages over conventional pyrometallurgy such as:

- The ability to produce copper locally at the mine site thus reducing transport costs and smelter charges,
- Better environmental compliance,
- The ability to produce copper at a lower cost,

For stirred tank systems, as a result of the nature of thermophilic bacteria and the operating environment, the capital and operating costs are increased as a result of:

- Corrosion: the materials of construction must be stainless steel or better,

- Low shear resistance of the bacteria: the tank sizes are large as a result of low pulp densities,
- High air demand: higher temperatures reduce the dissolved oxygen levels.

The GEOCOAT[®] process melds the advantages of stirred tank systems with the simplicity of conventional heap leaching. The process involves the coating of concentrates onto a suitable substrate, usually barren rock, then stacking the coated material in a conventional heap fashion. The heap is irrigated with acidic solutions containing iron and nutrients while low pressure ambient air is applied at the heap base.

The GEOCOAT[®] system has several advantages over convention pressure hydrometallurgical processes as well as stirred tank bioleaching:

- Lower capital and operating costs,
- The heap uses conventional plastic liners and irrigation systems,
- The lower resistance across the heap means air supply can be low pressure,
- Nutrient loads are recycled,
- The heap is a natural insulator so target operating temperatures are easily maintained,
- Solutions can be recycled to enhance the pregnant leach solution (PLS) grade,
- Simple operation means lower staffing and training levels,
- Smaller operations can afford the system,
- Reduced cutoff grade as a result of lower operating costs,
- Enhanced global metal recovery,
- Lowered cutoff grades,
- Less dependency on grade means the ability to treat lower grade concentrates and enhance the flotation recovery,
- Ability to utilize low grade material as support rock,
- Inherently safe due to the low pressure environment.

GeoBiotics, LLC has embarked on an extensive commercialization process for the GEOCOAT[®] process for chalcopyrite leaching. This program encompasses mathematical heap modeling, laboratory amenability and column tests, and large scale field trials. This paper documents the work that has been completed to-date including laboratory tests conducted at Lakefield Research Africa (Pty) Ltd, modeling compiled by the University of British Columbia and the ongoing investigation into heap parameters and effects of concentrate mineralogy including enargite.

2. THE GEOCOAT[®] PROCESS DESCRIPTION

The GEOCOAT[®] process incorporates elements of two successful and commercially proven technologies: heap leaching and biooxidation. Copper-bearing sulphide minerals are concentrated by flotation and thickened. The resulting slurry is thinly coated onto crushed, screened support rock, stacked on a lined pad, and allowed to biooxidize. Coating is accomplished by spraying the concentrate slurry onto the support rock as it discharges from the end of a stacking conveyor onto the biooxidation heap as shown in Figure 1. The coating solids density is highly dependent on the slurry viscosity and densities of 50-65% have been successfully coated at scale. The hydrophobic nature of the concentrate assists in the formation of a coating on the support rock. No binding agents are required.

The concentrate naturally adheres to the support rock and does not wash out of the heap during solution application or heavy rainstorms. A 30mm event was recorded over a half hour at a pilot heap test without consequence.

The support rock is relatively uniformly sized, in the range of 6 to 25 centimeters in diameter and the concentrate coating is relatively thin, less than one millimeter in thickness. The weight ratio of support rock to concentrate is in the range of 5:1 to 10:1. Figure 2 illustrates the concentrate coated support rock from a pilot test.



Figure 1. Coating Operation

Depending on the desired temperature of operation, the heap is inoculated with naturally occurring sulphide-oxidizing bacteria, such as the moderate thermophiles; *Acidithiobacillus caldus* (DSMZ strain 8584), *Sulfobacillus thermosulfidoxidans* (DSMZ strain 9293 and 11920), and the extreme thermophiles; *Acidianus brierleyi* (DSMZ strains 1651 and 6334), *Acidianus infernus*, (DSMZ strain 3191) *Metallosphaera sedula* (ATCC strain 3390) *Sulfolobus acidocaldarius* (ATCC strain 49426) *Sulfolobus shibatae* (DSMZ strain 5389) and *Sulfolobus metallicus* (DSMZ strain 6482).



Figure 2. Concentrate Coated Support Rock

Nutrients are added to the heap via recirculating solutions. As biooxidation progresses, the sulphides in the concentrate are oxidized and the solubilized copper, iron, arsenic and sulphate are carried from the heap by the recirculating solution. A portion of the solution stream is continuously bled from the circuit for purification and metal recovery.

The relatively uniform size of the support rock leads to large interstitial spaces within the heap and subsequently a low resistance to air and liquid flows. Sufficient air for biooxidation and heat removal is supplied to the heap by low-pressure blowers through a system of perforated pipes laid in the drain rock below the base of the heap.

After biooxidation additional lifts may be placed on the pad or the coated rock may be unloaded from the pad and the oxidized concentrate removed by trommeling or wet screening if precious metal recovery is warranted. The concentrate residue would be neutralized and then subjected to conventional recovery methods. The support can be recycled or, in the case of low grade sulphide ore, a portion can be bled out for disposal and replaced with fresh copper bearing ore.

3. GEOCOAT[®] COPPER DEVELOPMENT PROGRAM

GeoBiotics, LLC has embarked on an extensive development program to adapt the GEOCOAT[®] biooxidation technology for the extraction of copper from sulphide concentrates and low grade sulphide ores. The physical parameters surrounding the application of GEOCOAT[®] for biooxidation have already been proven in large scale field tests. This includes, coating, aeration, irrigation and concentrate residue recovery (Harvey *et al.*, 1999; Harvey and Potter, 1999; Harvey and Flemming, 1998). Additionally, the biooxidation parameters have been defined for gold bearing refractory sulphides at scale. Currently a test program is being conducted to provide the foundation for expanding the GEOCOAT[®] process to copper sulphides.

3.1. Laboratory Test Program

The laboratory program has been developed to provide insight into the mechanisms involved in the bioleaching of various copper sulphide minerals with the aim of maximizing the leach reaction rate and metal extractions. Investigations include complete mineralogical examination of both feed and residue samples, stirred tank biooxidation amenability testing, large scale column testing, preliminary downstream metal recovery and precious metal extraction. Additionally, adaptation of the specific inoculums is being conducted along with microbiological investigations.

Amenability tests are conducted in heated stirred reactors ranging in size from 10 liters to 40 liters. Aeration is supplied by cleaned compressed air. These reactors are capable of operating over a wide range of temperatures from 30°C to 80°C. A series of heated 6m high by 144mm diameter columns have been set up to facilitate the column testing. These columns are equipped with zone heating to ensure uniform temperatures. Low pressure humidified air is applied to the base of the column at rates in excess of stoichiometric.

Acid solutions are applied to the top of the heap via a peristaltic pump, the effluent solutions are collected separately at the heap base. Effluent solutions are generally recycled, however, solution is removed on a periodic basis to maintain the desired PLS profile. The column is fitted with sampling ports that allow for both solid and liquid sample removal. At the termination of the biooxidation cycle the column is acid/water rinsed, allowed to drain and then emptied. The concentrate residue is removed from the support rock by simple wet screening and the concentrate allowed to dry. All weights and volumes are recorded and all samples are assayed for the appropriate elements. Figure 3 shows the column setup at Lakefield Research Africa (Pty) Ltd.



Figure 3. Typical Large Scale Column Setup

The development program has been structured in a semi-factorial method using results from initial tests to dictate the subsequent test set. There are many variables surrounding the biooxidation of copper sulphides and this method of test design allows for quick optimization. The general program has been laid out in an effort to determine the influences of the following:

- Mineralogy,
- A variety of copper sulphide concentrates are being tested including two primary chalcopyrite concentrates, an enargite gold concentrate and a mixed copper sulphide gold concentrate,
- Inoculum/Temperature,
- A mixed inoculum has been adapted for the various temperature regimes under investigation including mesophiles, moderate and extreme thermophiles,
- A series of tests are being conducted that will determine the extent of copper extraction at each of the 3 temperature regimes for each concentrate type,
- Particle Size,
- A series of grind sizes are being tested to determine the rate controlling step in the leaching reactions,
- Oxygen Diffusion,
- A variety of oxygen concentrations are being applied to the tests ranging from 21% to 100% O₂,
- Heap Height,
- Tests are being conducted at a variety of simulated heap heights to determine the role of height on vertical variations in solution chemistry,
- Solution Chemistry,
- Solutions compositions are varied through recycle and discard or S/X to achieve the desired PLS concentrations,
- Locked-cycle testing is being conducted to model full scale heap operation.

3.2. Preliminary Results

Currently the copper development program is ongoing and as such only preliminary results are available. At present four columns have completed their biooxidation cycle while seven others are in process along with three stirred tank amenability tests. A total of 20 columns are planned.

As mentioned, a series of concentrates are under investigation. The first four columns focused on Concentrate A and the balance were initiated on Concentrate B. Table 2 shows the chemical and estimated mineralogical composition of these concentrates.

Table 2.
Chemical and Mineralogical Analysis

Element/Mineral	Composition (%)	
	A	B
Cu	26.1	25.8
Fe	29.7	31.9
S ²⁻	29.0	35.1
SO ₄	0.98	0.5
Au (g/t)	12.0	4.5
CO ₃ ²⁻	0.5	0.05
CuFeS ₂	78.0	75.0
FeS ₂	4.0	15.0
FeS	7.0	Trace
acid sol. Cu	1.5	N/D
acid sol. Fe	2.1	N/D

The primary copper carrying sulphide in both of these concentrates is chalcopyrite. A difference does exist in the amount of iron sulphide present. Mineralogical investigations of Concentrate A indicate that much of the iron sulphide (63%) may actually occur as pyrrhotite.

Visible gold occurs as relatively large grains with some telluride present. Fine grained gold is also present in intimate association with the sulphide matrix. Mineralogy on Concentrate B indicates that the main iron sulphide is pyrite with minor pyrrhotite. Gold is present in visible grains but also within fractures of the sulphide minerals.

3.2.1. Copper Extraction

Figure 4 shows the course of metal extraction during the biooxidation of Concentrate A. This particular column was initiated at 70°C with an preliminary acid rinse until the pH was below 2 followed by inoculation with an adapted mixed thermophile culture. As indicated there is an initial lag phase of approximately two weeks before any significant chalcopyrite biooxidation occurs. The biooxidation then progresses rapidly over the next 70 days at a rate of 1.14% copper extracted per day. The rate then decreases as the sulphides are consumed. The overall rate for the test was 0.70% per day including the lag period. After 140 days a total copper extraction of 97.5% was achieved based on solution assays. This extraction was confirmed by analysis of the solid residues which indicated a total extraction of 94.0%.

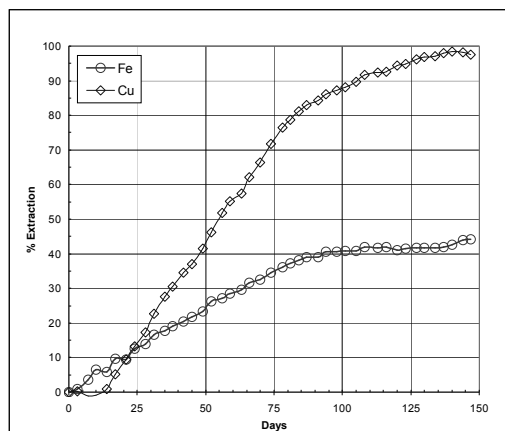


Figure 4. Metal Extraction from Chalcopyrite Concentrate A

The nature of this concentrate requires that near complete oxidation be achieved to achieve high copper extractions as indicated by Figure 5. This data is a compilation of completed test data derived from solid samples taken from various column locations and time intervals. As indicated a near linear relationship exists when the copper extraction is plotted against the sulphide biooxidation.

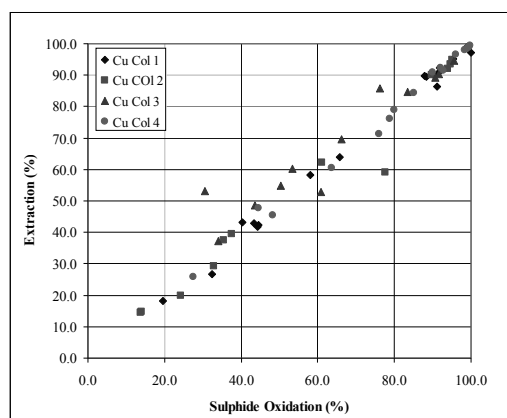


Figure 5. Copper Extraction vs. Sulphide Oxidation for Four Concentrate A Columns

Results from the tests on Concentrate B indicate that the copper extraction rate approximates that of the first Concentrate A column. Figure 6 shows the copper and iron extraction of Concentrate B. The current average copper extraction rate is approximately 0.70% per day with peak extractions exhibited of 1.4% per day. A similar linear trend is found between sulphide oxidation and copper extraction. This column is still under leach at the time of writing.

Both concentrates, when oxidized under thermophilic conditions, show near complete sulphide oxidation and yet the iron extraction to solution is much less than would be expected. Examination of the residues has found that, although near complete oxidation of the iron sulphides was achieved, 40-60% of the iron oxidized remained in the residue as a jarositic precipitate. This has several important implications. Firstly, it reduces the iron that has to be treated and disposed of from the PLS and secondly, its formation releases acid to the PLS solution. There is one potential drawback; that the formation of iron precipitates could cause occlusion of the residual gold making subsequent recovery more difficulty. This is examined in detail below.

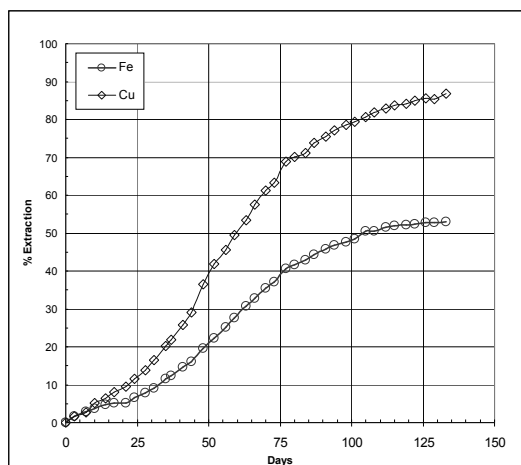


Figure 6. Metal Extraction from Chalcopyrite Concentrate B

3.2.2. Temperature Dependence

Heat balance modeling of Concentrate A has indicated that a period of 14 to 21 days would be required for the heap to reach operating thermophilic temperatures (Peterson, 2002; Dixon, 2000; Dreisinger and Dixon, 2002). This was calculated using very small length columns. Since heap heat up is an extremely important factor it was decided to test these results on the large scale columns.

A series of two columns were established to determine the amount of copper that could be solubilized in a given temperature regime. The first column, established with the same parameters as the column discussed above, was inoculated with mesophiles and held at 35°C until no further copper was extracted, the column was then ramped to 50°C and inoculated with moderate thermophiles and held until no further copper was extracted. Finally, the column temperature was increased to 70°C and inoculated with extreme thermophiles as shown in Figure 7. The second column was treated in a similar fashion except that it was started at the moderate thermophile level as shown in Figure 8. It is envisioned that some heaps may ramp very quickly through the mesophile range thus obviating the use of mesophiles.

Figure 7 shows the biooxidation of Concentrate A under the three temperature regimes. At 25 days the copper extraction rate began to slow down and the column was ramped to 50°C, at 53 days the rate again slowed and the column was ramped to 70°C. Figure 8 shows a similar trend but the column was started at 50°C in the moderate thermophile range. After 26 days the column temperature was elevated to 70°C as the copper extraction had slowed.

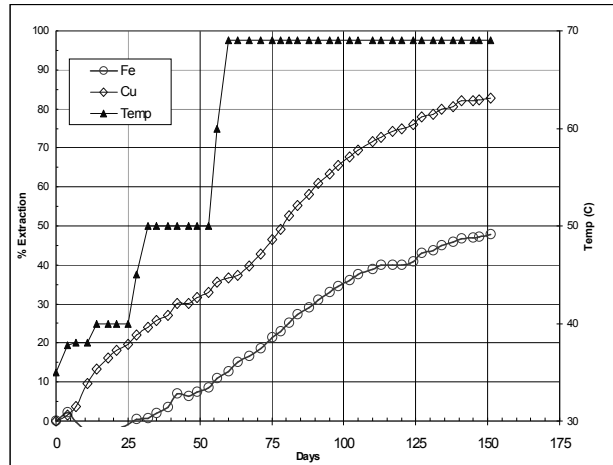


Figure 7. Mesophile, Moderate and Extreme Thermophile Biooxidation

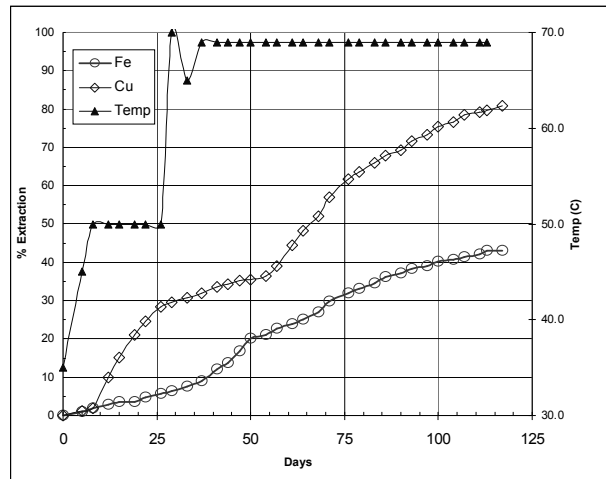


Figure 8. Moderate and Extreme Thermophile Biooxidation

These columns have completed their biooxidation cycle and achieved similar copper extractions to the first column shown in Figure 4. The column exposed to the three temperature regimes achieved 93.4% copper extraction while the second column operated at only the two temperatures achieved 91.4%. These columns were not allowed to go to ultimate completion due to resource constraints in the laboratory. It is significant that both columns were able to achieve high ultimate extractions of copper despite having been subjected to passivation. Mineralogical analysis did not identify any additional passivating elements beyond those normally found in the residue, namely jarosite. The length of time under biooxidation for these columns is not significant due to the imposed lag times between inoculations and temperature increases.

It is obvious from this data that the chalcopyrite Concentrate A can not be effectively biooxidized under mesophilic or moderate thermophilic temperature regimes in a heap environment a finding consistent with most literature (Hackl *et al.*, 1995; Third *et al.*, 2000). However, enough iron sulphide and copper sulphide can be oxidized at lower temperatures to enable the heap to obtain extreme thermophilic temperatures. Additional modeling will be conducted using this data to verify these results. A large scale demonstration heap is planned in the near future to show conclusively that adequate temperatures can be achieved to maintain thermophilic biooxidation.

3.2.3. Gold Extraction

Since many chalcopyrite concentrates contain significant quantities of precious metals, the ability to recover these metals after biooxidation is economically important. Concentrate A is the only concentrate residue that has been subjected to CIL testing to-date and three residues have been tested. The first residue is from the column operated at thermophilic temperatures only (Figure 4), the second is from the column operated at the three temperature regimes (Figure 7) and the final is from a test where the temperatures were ramped through to thermophilic levels in two weeks (not shown). The initial feed concentrate had a gold grade of 12.0g/t with negligible silver. After biooxidation the residue gold grade had increased to 20.8 to 26.5g/t depending on the weight loss incurred. The sample loss varied from 47% to 50%. Mass loss will vary during biooxidation depending on the concentrate and the amount of iron precipitated in the heap. In the case of Concentrate A, although oxidations ranged from 91.6% to 98.0% (sulphide), iron solubilization ranged only from 48.2% to 57.4%. The precipitation of iron within the heap provides the advantage of having less iron to treat in the downstream processes. However, this precipitated iron could cause problems in the form of mineral occlusion. It is evident from the test that the precipitated iron did not adversely impact the copper extraction.

Both Concentrate A and B can not be subjected to conventional CIL processing without first being biooxidized as the cyanide consumptions are extremely high and the gold recovery very low. Biooxidation liberates the gold and removes the copper so the gold should be relatively free leaching in a conventional CIL plant. Additionally, the process of recovering the concentrate from the support rock helps to rinse the residue prior to cyanidation reducing the presence of cyanicides. Table 3 shows the initial CIL gold extraction for Concentrate A feed and biooxidation residue.

Table 3
 Preliminary Gold Extractions – Concentrate A

Sample	Conditions NaCN	Time (hr)	Reagent Consumption		Grade Au		Gold Dissolution (%)	Oxidation (%)
			Lime (kg/t feed)	NaCN (kg/t feed)	Feed (g/t)	Residue (g/t)		
Feed	2000ppm	24	49.9	49.9	12	9.3	25	0
Test 1 – Final	2000ppm	24	9.7	28.8	20.8	5.12	75.3	91.6
Test 1 – Final	2000ppm	72	9.4	37.3	20.8	1.49	92.8	91.6
Test 1 – Final	2000ppm – Regrind	72	8.0	62.4	20.8	0.83	96	91.6
Test 2 – Final	2000ppm	72	11.2	31.6	25.5	1.7	93.4	94.6
Test 2 – Final	2000ppm – Regrind	72	11.5	37.2	25.5	1.5	94.3	94.6
Test 3 – Final	2000ppm	24	5.5	8.6	26.5	3.39	87.2	98
Test 3 – Final	10000ppm	24	4.1	12.5	26.5	0.82	96.9	98

As shown by Table 3 there is a direct correlation between oxidation, gold extraction and cyanide consumption. With increasing oxidation the gold extraction increased and the cyanide consumption decreased. This is likely for several reasons. Increasing oxidation correlates to increasing gold liberation and also reduced deleterious biooxidation products in the residue such as elemental sulphur. It was found that at lower oxidation levels high gold extractions could be achieved by increasing the retention time, regrinding or increasing the cyanide levels. Much more work is planned for the optimization of the gold recovery portion of the circuit but preliminary results indicate that high gold recoveries can be achieved with moderate reagents consumptions as long as the oxidation level is high >92%.

4. CONCLUSIONS

The GEOCOAT[®] process possesses many inherent advantages over conventional pyrometallurgical methods for copper extraction. Additionally, the melding of conventional heap leaching with biotechnology provides further advantages over other hydrometallurgical processes.

GeoBiotics, LLC proprietary GEOCOAT[®] technology is being successfully applied to chalcopyrite on the laboratory scale. Copper extractions in excess of 97% have been achieved under thermophilic conditions. Work is continuing on defining the system parameters including enhancing the leaching kinetics, downstream processing, and precious metal recovery. A large scale demonstration heap will be the culmination of this program.

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