Bioleaching of base metal sulphide concentrates: A comparison of high and low temperature bioleaching

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Synopsis

Billiton Process Research has carried out extensive research over the past four years to develop new process technology using bioleaching for extraction of copper and nickel from their sulphide concentrates. Continuous pilot scale and laboratory batch testwork has been carried out with adapted mesophile bacterial cultures at 40°C–45°C, moderate thermophile cultures at 50°C–55°C and thermophile cultures at 65°C–85°C.

Pilot scale work has demonstrated the commercial viability of mesophile cultures for bioleaching of secondary copper sulphide and nickel sulphide concentrates. Moderate thermophiles offer benefits in terms of reduced cooling requirements for commercial reactors and, in the case of bioleaching of nickel concentrates, some selectivity over bioleaching of pyrite. Continuous pilot scale testwork has shown that thermophiles achieve efficient bioleaching of primary copper sulphide and nickel sulphide concentrates, giving much higher recoveries than achieved by bioleaching with a mesophile or moderate thermophile culture.

Introduction

Billiton Process Research is committed to developing bioleaching for the extraction of metals from base metal sulphide concentrates. Bioleaching is particularly suited to the processing of low grade copper and nickel concentrates, or copper concentrates containing arsenic, which are not suitable for treatment by conventional smelting.

As part of the development programme, moderate thermophile and thermophile cultures have been sourced, and laboratory and pilot scale testwork has been carried out to assess the application of these cultures for the bioleaching of copper and nickel sulphide concentrates. The work presented in this paper discusses some results of this research and draws a comparison between the performance of the different cultures for commercial bioleaching operations.

Characterization of the bioleaching micro-organisms

Mesophile bacterial culture

The adapted mesophile bacterial culture, developed at Billiton Process Research, has been characterized by the microscopic immunofluorescence technique[1] as well as the PCR technique[2]. The principal bacteria present in continuous culture have been found to be *Leptospirillum ferrooxidans, Thiobacillus thiooxidans* and *Thiobacillus caldus. Thiobacillus ferrooxidans*, although present in the culture, does not normally occur in significant numbers, probably due to operation at temperatures of 40°C–45°C. At operating temperatures of greater than 42°C, *Thiobacillus caldus* is the dominant sulphur oxidizing bacterium.

Moderate thermophile culture

A mixed culture of moderately thermophilic bacteria has been successfully adapted to bioleaching of nickel sulphide concentrates. Characterization of the culture by analysis of 16S rDNA sequences of the population indicated that species of *Acidimicrobium* and *Sulfobacillus* appeared to be the principal iron-oxidizing bacteria and *Thiobacillus caldus* was the principal sulphur-oxidizing bacterium[3]. Optimum growth appears to occur at an operating temperature of 50°C but effective bioleaching has been achieved at temperatures up to 55°C.

Thermophile cultures

The thermophiles adapted to sulphide mineral leaching are *Sulfolobus*-like archaea. Two cultures have been successfully adapted to copper and nickel sulphide mineral leaching, a 68°C culture, operating in the range 65°C–70°C, and a 78°C culture, operating in the range 75°C–85°C. The 68°C culture, isolated by Billiton Process Research, is most probably of the type *Sulfolobus metallicus*. The

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78°C culture has not been fully characterized, it was provided by Paul Norris, University of Warwick, UK.

Bioleaching of copper sulphide concentrates

Comparison of bioleaching with mesophile and thermophile cultures

Extensive laboratory and continuous pilot scale testwork has shown that the mesophile culture, adapted to copper sulphide concentrates, is able to attain complete dissolution of most secondary copper sulphide minerals including chalcocite, covellite, bornite and enargite. Generally, it has not been successful for bioleaching of chalcopyrite, due to passivation of this mineral during leaching.

The required grind size to achieve complete mineral dissolution is typically a d_{80} of 38 μm. Finer grinding to a d_{80} of 25 μm may improve the leachability of refractory sulphide minerals such as enargite. Ultrafine milling to 100% passing 10 μm will enhance chemical leaching but, based upon operating experience at Billiton Process Research, does not enhance bacterial leaching.

The relative rates of copper sulphide mineral dissolution are shown in Figures 1 and 2, for bioleaching of a Zambian and a Chilean concentrate with the adapted mesophile culture. The Chilean concentrate was pre-treated prior to bioleaching, by leaching in an iron(III) sulphate solution; this simulates pre-leaching with recycled bioleach product liquor. The pre-treatment resulted in 98% dissolution of chalcocite, 78% dissolution of cubanite, 57% dissolution of bornite, 30% dissolution of chalcopyrite and 4% dissolution of enargite. These results are indicated in Figure 2, as the mineral dissolution at time zero, for the continuous bioleach.

The composition of the two concentrates prior to leaching is given in Table I.

The results presented in Figures 1 and 2 indicate that the preferential order of mineral bioleaching with the mesophile culture is:

Chalcocite>Bornite>Cubanite>Covellite>Pyrite>Enargite>Carrolite>>Chalcopyrite

Bioleaching of the Zambian concentrate showed that the rate of carrollite ($Cu(Co,Ni)_2S_4$) dissolution increases in the final stages of the continuous bioleach which corresponds to an increase in the solution redox potential above 580 mV versus a standard calomel electrode (SCE). Achieving a higher redox potential in the first stage of the continuous bioleach may be expected to improve the dissolution of carrolite significantly. The overall copper dissolution achieved was 88%. The residual copper was present mainly as chalcopyrite and its dissolution was limited to 43%.

Continuous bioleaching of the Chilean concentrate resulted in high dissolutions of all the secondary copper sulphide minerals. The overall copper dissolution achieved was 93%. The chalcopyrite dissolution was limited to 45%. The enargite dissolution was 79%.

In both concentrates, the partial dissolution of chalcocite resulted in the formation of covellite, as a reaction product. This effect resulted in the apparent lack of dissolution of covellite in the first two days of continuous bioleaching.

In order to achieve dissolution of enargite and carrollite, high solution redox potentials are required[4]. The solution redox potential is determined by the iron(III)/iron(II) concentration ratio. During bioleaching, rapid chemical leaching of secondary sulphide minerals results in the reduction of iron(III) to iron(II), as shown by the following reaction for chemical leaching of chalcocite to form covellite:

$$Cu_2S + 2Fe^{3+} = CuS + Cu^{2+} + 2Fe^{2+} \qquad [1]$$

In the early stages of bioleaching of a secondary copper sulphide concentrate, the rate of chemical reduction of iron(III) to iron(II) often exceeds the rate of bacterial oxidation of iron(II) to iron(III). The net result is a low solution redox potential in the bioleach due to high concentrations of Fe(II) in solution.

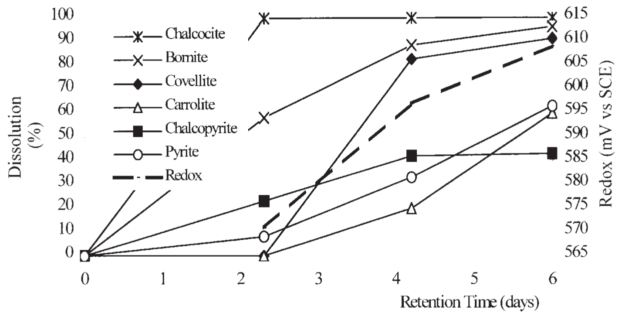

Figure 1—Continuous bioleaching of a Zambian concentrate with the mesophile culture at 40°C

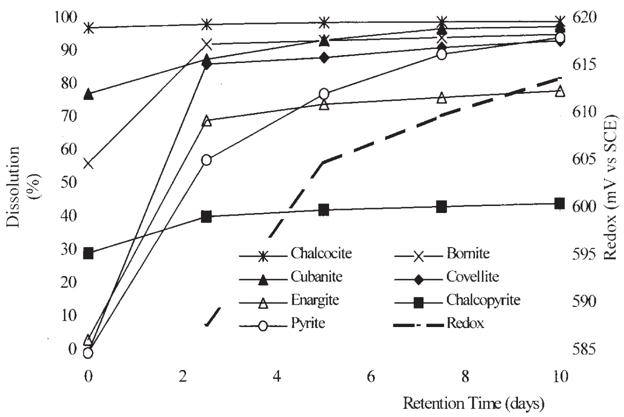

Figure 2—Continuous bioleaching of a Chilean concentrate with the mesophile culture at 40°C

Table I

Composition of the Zambian and Chilean concentrates

Composition (%)	Zambian concentrate	Chilean concentrate
Copper	18	35
Chalcocite	12.4	20.3
Bornite	2.6	1.9
Cubanite	0.4	-
Covellite	4.6	10.2
Carrolite	0.5	-
Chalcopyrite	7.4	3.1
Pyrite	4.9	36

The secondary sulphide mineral content of the concentrate may be effectively lowered by carrying out a chemical pre-leach to remove easily leached minerals such as chalcocite. The pre-leach may be carried out using recycled acidic bioleach product liquor, after copper removal by solvent extraction. The effect is to lower the rate of iron(III) reduction by chemical leaching in the subsequent bioleach, allowing higher redox potentials to be maintained.

Flotation testwork on the bioleach residue has shown that the residual chalcopyrite may be recovered from the residue by froth flotation, to produce a concentrate acceptable for further treatment by conventional smelting. Results of laboratory tests on a Chilean bioleach residue containing 9.3% copper, indicated a copper recovery of 94% was achieved, producing a concentrate assaying 15.9% copper.

The bioleaching of chalcopyrite has been successfully achieved in batch and continuous culture using both the 68°C and 78°C thermophile cultures. Results of typical batch tests are presented in Table II.

In order to develop continuous bioleaching of primary copper sulphide concentrates using thermophile cultures, a continuous 1040 litre pilot plant was constructed at Billiton Process Research in September 1997. The plant consists of two 240 litre and four 140 litre stirred tank reactors, connected in series. The plant has been in operation since November 1997.

The pilot plant is equipped with a sophisticated computer controlled mass flow control and gas analyser system. The system is used to determine the inflow and outflow of oxygen and carbon dioxide. From the measured data, gas utilizations may be calculated and used to estimate mineral oxidation rates and cell growth rates.

The pilot plant was inoculated with the 78°C thermophile culture in April 1998 and was operated continuously treating a Chilean chalcopyrite concentrate at a slurry feed solids concentration of 10% by mass. The concentrate contained 85% chalcopyrite and had a copper content of 31%. Results obtained are shown in Figure 3.

The results indicate that a copper dissolution of 98% is attained at a total residence time of 5 days. A dissolution of 82% was obtained in the first stage of the pilot plant, corresponding to a residence time of 1.8 days. These results are very positive compared to mesophile bioleaching where the copper dissolution was limited to less than 30%.

The retention time required in continuous bioleaching is significantly lower than the batch treatment period required to attain the same degree of mineral leaching. This effect has been noted previously in bioleaching of refractory gold ore concentrates[5]. Future continuous pilot plant operation will test the ability of bioleaching to recover from process disruptions such as a failure of the air supply.

Table II

Batch bioleaching of chalcopyrite concentrates with thermophiles

Concentrate	% Chal-copyrite	% Secondary sulphides	Culture	Treatment period (days)	Copper dissolution (%)
Chile 2	4.3	14.2	68	30	96
Zambia 1	23	41	78	33	97
Zambia 2	11	30	68	42	95
Australia 1	55	-	68	23	96

Implications for commercial bioleaching

Bioleaching with the mesophile culture is robust and the requirements for scale-up and engineering design are well understood by Billiton, from its experience of BIOX®, technology[6]. Development work at Billiton Process Research has shown that similar technology may be applied to bioleaching of secondary copper sulphide concentrates.

Bioleaching with mesophiles creates an opportunity to treat low grade concentrates or concentrates containing arsenic in the form of enargite, neither of which are suitable for processing by conventional smelting.

Bioleaching of secondary copper sulphides with the adapted mesophile culture is at an advanced stage of development. An engineering design is currently being prepared for a commercial demonstration plant to be built in Chile.

The principal limitation of mesophile bioleaching for treatment of copper concentrates is the inability to leach chalcopyrite efficiently.

The pilot scale results presented in this paper show that cultures of *Sulfolobus*-archae are effective in bioleaching primary (chalcopyrite) copper concentrates in continuous culture, using stirred tank reactors. Relatively high rates and extents of chalcopyrite dissolution have been achieved compared to bioleaching with a mesophile culture. Billiton Process Research will continue to develop continuous bioleaching with thermophiles, with the objective of demonstrating the technology at a commercial scale.

Bioleaching of nickel sulphide concentrates

Comparison of batch bioleaching with mesophile, moderate and thermophile cultures

Laboratory batch testwork has established the amenability of a variety of nickel sulphide concentrates to bioleaching with adapted mesophile cultures. The variety of concentrates tested and the nickel dissolutions attained are shown in Figure 4. The principal nickel sulphide mineral in all the concentrates is pentlandite and associated minerals are pyrrhotite and pyrite.

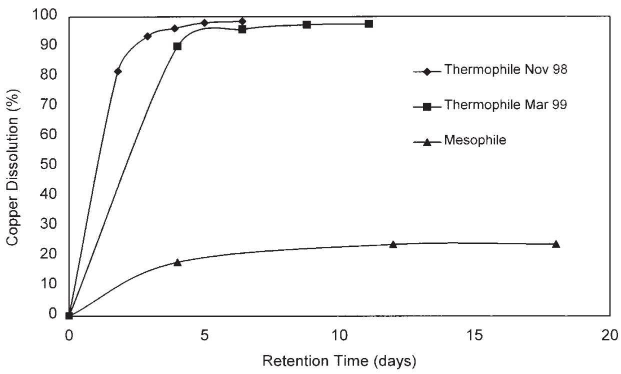

Figure 3—Continuous bioleaching of a chalcopyrite concentrate with the 78°C thermophile culture

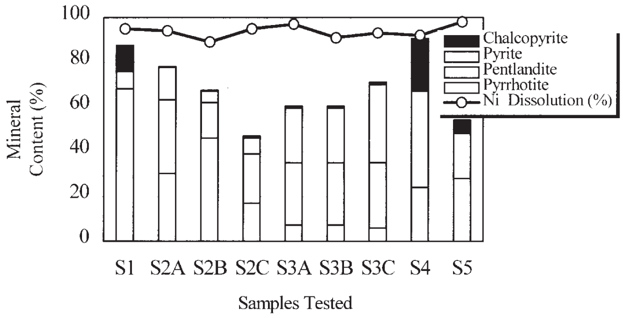

Figure 4—Batch bioleaching of nickel sulphide concentrates with an adapted mesophile bacterial culture

Despite the variation in concentrate grades and the relative proportions of the principal sulphide minerals present, batch bioleaching with the adapted mesophile culture consistently attained nickel dissolutions of 92% to 96%.

The S3C concentrate has been used as a reference sample to optimize the bioleaching process and to compare bioleaching by mesophiles at 40°C–45°C with moderate thermophiles at 50°C–55°C and with thermophiles at 65°C–85°C.

The results of comparative batch tests using mesophile cultures or moderate thermophile cultures, indicate that bioleaching leach rates are similar. However, a degree of selective leaching of pyrrhotite and pentlandite over pyrite occurs during bioleaching with the moderate thermophile culture. Thus higher nickel recoveries may be attained for the same extent of sulphide removal. Bioleaching with an active thermophile culture results in rapid leaching of all the sulphide minerals present in the concentrate so that selective leaching is not apparent.

Test results showing the correlation between nickel dissolution and sulphide removal for bioleaching with mesophile, moderate thermophile and thermophile cultures are presented in Figure 5. The selective leaching of pentlandite achieved by batch bioleaching with the moderate thermophile culture is evident. The solid line in Figure 5 indicates the theoretical relationship between nickel dissolution and sulphide removal, assuming no pyrite is leached.

Continuous pilot scale results, for bioleaching of the S3C concentrate with the mesophile and the 68°C thermophile culture, are presented in Figure 6.

From Figure 6, it is evident that bioleaching of pentlandite with mesophiles is relatively slow. A retention time of over 8 days was required for continuous leaching of the S3C concentrate to attain a nickel recovery of 93%. Bioleaching with the 68°C thermophile culture shows much improved leach kinetics, resulting in a higher nickel recovery. A nickel recovery of 98% was achieved in a retention time of 4 days. It should be noted, however, that continuous operation with the mesophile culture was with a feed solids concentration of 15% by mass, compared to 10% for the 68°C thermophile culture. The improved nickel dissolution is confirmed by the bioleach residue analysis presented in Table III.

The results indicate that much greater rates of sulphur oxidation are achieved in the thermophile bioleach. The final residue product of thermophile bioleaching is also more acceptable for disposal to the environment, due to its much lower metal content.

Implications for commercial bioleaching

Bioleaching with mesophiles, as part of the BioNIC®, process, has been demonstrated at pilot scale to be economically viable for commercial application[7]. The use of moderate thermophiles may offer further advantage in terms of selective bioleaching and possibly increased recoveries in continuous operation. The recent pilot testwork indicates that

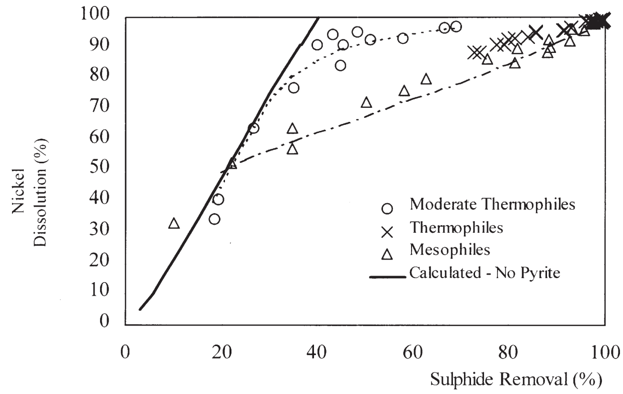

Figure 5—Correlation between nickel dissolution and sulphide removal for bioleaching of S3C concentrate

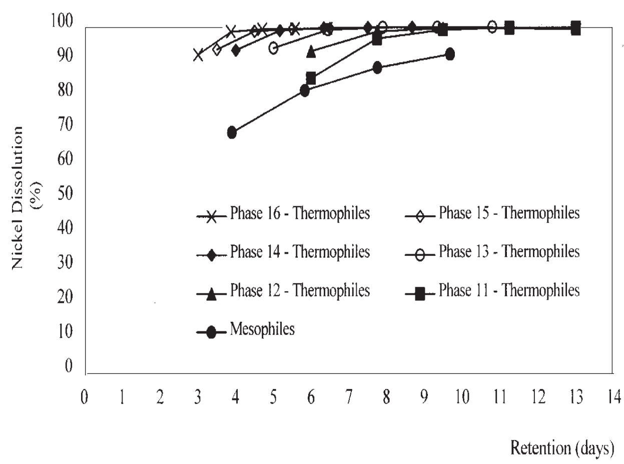

Figure 6—Continuous bioleaching of S3C concentrate with the mesophile and 68°C thermophile cultures

Table III

Residue analysis for continuous bioleaching of S3C concentrate

Element (%)	Thermophiles	Mesophiles
Nickel	0.08	1.90
Copper	0.08	0.49
Sulphide	0.10	4.30
Sulphur	<0.2	3.30

bioleaching with thermophiles will result in faster leach kinetics and significantly higher nickel recoveries. Future development work will continue with the objective of developing thermophile bioleaching to a commercial scale.

Conclusions

Research at Billiton Process Research has shown that bioleaching of secondary copper sulphide and nickel sulphide concentrates with adapted mesophile bacterial cultures is technically feasible. The BioNIC®, process for treatment of nickel concentrates has been demonstrated and shown to be economically viable[7]. Bioleaching is particularly suited to treatment of low grade concentrates, or concentrates containing deleterious elements such as arsenic.

Moderate thermophiles perform similarly to mesophile cultures but may afford selective leaching of pentlandite over pyrite and, in continuous culture, may be expected to achieve slightly higher metal recoveries for the same plant retention time.

Continuous bioleaching with thermophile cultures has produced encouraging results, which indicate the ability to attain high leach rates and significantly improved metal recoveries for bioleaching of primary copper and nickel sulphide concentrates. Development of bioleaching with thermophile cultures will remain a priority at Billiton Process Research, with the objective of developing commercial processes.

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Aeromix Process Systems signs assay and test work agreement with Mintek*

An agreement to co-operate on attrition scrubbing and the process equipment development, test work and analysis has been signed between process specialists Aeromix Process Systems and Mintek South Africa.

'An example of work that will be carried out in conjunction with Mintek, is that if a client has heavy minerals sands deposits and needs to determine the effectiveness of attrition scrubbing, Mintek will conduct the test on our behalf,' says Mark Craddock, director of Aeromix.

'We do not have the capacity to do full test work and in exchange for utilizing Mintek's facilities, they will make full use of our extensive pilot plant equipment'.

The major reason behind this is to develop local designs and manufacture process equipment that is pertinent to local conditions.

'Gone are the days that our mining and minerals industry has to be in awe of overseas technology,' says Craddock, 'we need local expertise for local conditions and to boost South African products'.

The company intends to tailor-make process systems to suit customer specification and the nature of the product being mined. An example would be a customized attrition scrubber to suit specific retention times and pulp density. Mintek will be doing comparative and optimization tests on Aeromix equipment.

Optimization and tests are currently being carried out on the company's newly patented 'Flotrition' that is due for launching once this has been completed.

Mintek has the capacity to conduct bench scale and pilot plant attrition scrubber test work on equipment that is fitted with a variable speed drive allowing exact measurement of optimal power inputs.

The purchase of this particular pilot plant led to the agreement between the two companies being initiated.

Aeromix Process Systems, with its focus on attrition scrubbers is now in the forefront of design globally. The company has the backing of the internationally renowned Lightinin range of products, which has the in-house capacity to conduct computational fluid dynamics. This is the ability to work out the flow patterns within the machines and optimize the inter-particle rate of collusion.

To date test work has been conducted on platinum dump material, phosphate and heavy mineral sands.

For further comment contact Mark Craddock, Aeromix (011) 608-0477. ◆

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