

## **Leaching of a low-grade, copper-nickel sulfide ore. 2. Impact of aeration and pH on Cu recovery during abiotic leaching**

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### **Abstract**

The conditions under which copper was retained and re-distributed in a test heap of pyrrhotite-rich, copper-nickel sulfide ore were investigated in abiotic column leaching tests. It was determined that acidity plays a key role in maximising copper recovery. During passage through the ore bed, when the leachate pH rose to >2.3, copper ions previously released to solution through the oxidation of chalcopyrite were retained by adsorption on, or reaction with, ore minerals. Lack of aeration (limited oxygen) had only a small impact on copper recovery, in association with a favourable pH environment. Possible reaction mechanisms are discussed. The results indicated the need for careful acid management in the operation of heaps of pyrrhotite-rich ores such as complex copper-nickel sulfide ores.

Keywords: Chalcopyrite; Pentlandite; Pyrrhotite; Leaching

## 1. Introduction

Heap leaching technology is used for the extraction of metals from low grade ores such as copper oxides and secondary copper sulfides and is currently being trialed for primary copper sulfides, nickel laterites and copper-nickel sulfides (Clark et al., 2006; Cann, C., 2007; Watling, 2006; 2008). When sulfide ores are heap leached, native and/or introduced bacteria assist the process, mainly through their ability to oxidise iron(II) to iron(III) and reduced-sulfur species to sulfate. In this way they regenerate the ferric ion oxidant required for the oxidation of sulfide minerals and provide some additional acid within the heap.

Following substantial smaller-scale test work on a disseminated copper-nickel ore from the Mt Sholl deposit, Western Australia, a 5000 t test heap was constructed and operated at the Radio Hill mine near Karratha (Watling et al., 2009). In about one year of operation, 90% of the contained nickel but only 50% of the contained copper were leached into solution. Copper extraction lagged behind that of nickel by 5-6 months. At the time, it was hypothesized that lack of oxygen in some parts of the heap might have caused the leach chemistry to change and some solubilised copper to be re-deposited. Heap samples collected by auger from different depths were subjected to a diagnostic leach and the content of non-chalcopyrite copper species determined. The results indicated strongly that copper had re-deposited in the heap, mainly at about 1-3 m depth (Table 1).

The reasons for the observed copper re-deposition were investigated using copper-nickel sulfide ore obtained from the Mt Sholl deposit (Western Australia). Preliminary bioleaching experiments were conducted including studies on acid conditioning, inoculation and aeration (Watling et al., 2009). Results obtained for inoculated columns indicated that the absence of aeration had a negative effect on nickel and copper extraction. The consistently low potentials of solutions discharged from the unaerated column indicated that ferrous ion biooxidation was restricted. The presence of elemental sulfur in leached residues in aerated columns indicated inefficient sulfur biooxidation, possibly a consequence of high leachate pH (Plumb et al., 2008). High leachate pH had an indirect effect on copper recovery by promoting conditions favourable to the formation of insoluble iron-oxy-hydroxy-sulfate compounds, thus depleting the ferric ion concentration required to oxidise sulfide minerals and creating a substantial layer of 'scale' on particle surfaces.

In this study, the results of which were first presented at the AusIMM Bac-Min Conference (Maley et al., 2004), the impact of oxygen depletion on copper recovery was investigated in more detail in four abiotic leaching columns operated in series. The impact of varied feed solution pH on leach chemistry was also investigated in abiotic columns operated in parallel. In addition, ancillary small-scale flask tests using pulverised ore provided corroborative data and assisted in the interpretation of results.

## **2. Materials and Methods**

### *2.1. Copper-nickel sulfide ore*

The ore, from the Mt Sholl deposit, near Karratha, Western Australia, was crushed and screened and particles in the size range  $-6.7+4.75$  mm were used in all column experiments.

A representative sample of the ore was pulverised for ancillary flask tests and for chemical and mineralogical analysis using the Rietveld refinement of X-ray diffraction (XRD) data (Watling et al., 2009). The ore was comprised primarily of silicate minerals, augite (48%), amphibole (actinolite with magnesianhornblende - 24%) and chlorite (10%), with minor phases quartz and albite. The sulfide minerals were pyrrhotite (11%), chalcopyrite (2-4%), and pentlandite (1-2%). The pyrrhotite, with formula  $Fe_{1-x}S$  where  $x$  varies between 0 and 0.125, but denoted as FeS in this paper, contained about 8,500 mg Ni/kg.

Sulfide mineral associations and liberation in whole ore particles were also determined previously using QEMSCAN (Watling et al., 2009) and showed that in this ore, pyrrhotite is mainly associated with the chlorite and the other silicate minerals, with overall 8% exposure on particle surfaces. Pentlandite is associated (25%) with pyrrhotite but is largely (~40%) encapsulated within the silicate matrix and only about 1-1.5% is exposed on particle surfaces. Chalcopyrite is mainly associated with chlorite and the silicate matrix and occurs as both disseminated particles ( $<50$   $\mu\text{m}$ ) and larger particles (up to 300  $\mu\text{m}$  diameter), with only about 3% surface exposure.

### 2.3. *Abiotic column leaching – Impact of oxygen depletion*

The effect of aeration on the re-deposition of copper from solution onto the copper-nickel ore was investigated using two sets of four linked polypropylene columns (Figure 1). All columns were contained within temperature controlled water baths maintained at 45°C. One set of columns was aerated continuously at 0.5 L/min, while the other set was not aerated. Each column was loaded with copper-nickel ore (approximately 5.3 kg of size fraction -6.7+4.75 mm). Prior to loading, each column charge was wetted with dilute sulfuric acid (450 mL, pH 1.8) for 5 minutes in a cement mixer to bind any fine particles to the larger particles. The loaded columns were allowed to drain overnight before irrigation was commenced.

The first column in each set was irrigated with a pH 1.8 synthetic leach solution (Table 2) drawn from an ambient-temperature reservoir (18 L). Nickel, copper and iron concentrations in the irrigation feed were similar to those obtained during the bioleaching of the ore in a stirred, agitated tank. Sodium benzoate (0.1 g/L) was added to the reservoir to suppress the growth of any contaminant bacteria present in the solution or ore. The solution was delivered to and pumped from the columns at 1.0 mL/min using a peristaltic pump.

The solution reservoir from each set of columns was periodically stirred and sampled (approximately 2 mL). A sample (approximately 1 mL) of the discharge solution from each column was also collected. The volume remaining in the reservoir was recorded after each sample was taken, and where necessary the pH was adjusted to 1.8 using concentrated sulfuric acid. The pH, redox potential and ferrous ion concentration were determined for all reservoir and column discharge samples. An aliquot of each reservoir sample (1 mL) was also mixed with concentrated hydrochloric acid (0.5 mL) and Cu, Ni and Fe concentrations in this solution were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

On day 36, an additional quantity of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.330g) was added to the solution reservoirs.

At the conclusion of leaching the columns were drained and rinsed with dilute sulfuric acid (pH 1.8) (two days) and then unloaded and the leach residues were dried at room temperature. Representative samples of each column residue were separated using a riffle splitter. These samples were pulverised in a ring mill, thoroughly mixed,

and then portions digested in aqua regia. The resulting solutions were analysed for copper, nickel and iron using ICP-AES.

#### 2.4. *Abiotic column leaching – Impact of solution pH*

The effect of solution pH on copper precipitation was investigated in similar columns operated in parallel, with solution recycle via separate reservoirs containing 8 L of leach solution. These columns were not aerated. Synthetic leach solutions without added ferric ion (Table 2) were prepared at pH levels of 1.0, 1.5, 1.8, 2.0, 2.5, 3.0 and 4.0. Columns were set up, maintained and monitored as described above.

#### 2.5 *Abiotic flask tests – Impact of solution pH*

Copper sulfate solutions (150 mL) of the selected copper concentration and pH were accurately weighed into clean, dry, sterile conical flasks. The total mass of each flask was recorded and a sample of solution (approximately 1.5 mL) was removed using a sterile pipette. The mass of the flask and solution was recorded. An accurately weighed 4 g sample of pulverised ore was transferred to the flask, which was weighed a third time. Flasks were placed in an orbital shaker operated at 180 rpm and 45 °C.

Water lost from the flasks by evaporation was replaced periodically by weighing the flask and adding sterile deionised water until the mass of the flask equaled its previous mass. The flask contents were shaken briefly and allowed to settle (5 min) before a 1.5 mL sample was removed using a sterile glass Pasteur pipette and transferred to a small centrifuge tube. After sampling, the pH of each flask was re-adjusted to the desired set point by the drop-wise addition of concentrated sulfuric acid. The flask was reweighed and returned to the orbital shaker.

The sample solution was centrifuged at 16,000 rpm for 10 min and the supernatant drawn off into a clean tube. The pH, solution potential and ferrous ion concentration were determined on the supernatant. In addition, a 1.0 mL aliquot was diluted with 0.5 mL of concentrated hydrochloric acid and this solution was analysed for Cu, Ni and Fe using ICP-AES.

At the conclusion of the experiment, the solid leach residues were separated from solution by passage through 0.45 µm pore-size membranes and rinsed with

dilute sulfuric acid of the same pH as the experimental leachate. The solids were dried at room temperature and stored for further analysis.

## 2.5. Analytical

Solutions were analysed for Ni, Cu and Fe using a Varian Liberty 220 ICP-AES. The plasma was located in the axial position, with a total sample uptake time of 18 seconds and a washout time of 15 seconds. Solid samples were digested in aqua regia before ICP analysis.

Ferrous ion concentrations were determined colorimetrically using a procedure adapted from [Wilson \(1960\)](#). A volume of the analyte solution (80  $\mu$ L) was added to an ammonium acetate buffer containing 2,2-dipyridyl (4 mL). The absorbance of the resultant pink solution was measured at 525 nm using a Cary 50 Bio UV-vis spectrometer, with the ferrous concentration determined via a previously established calibration curve. Where necessary, samples were diluted quantitatively with pH 2 sulfuric acid before addition to the dipyriddy solution to give an absorbance within the calibration range.

## 3. Results

### 3.1 Impact of oxygen limitation on abiotic leaching

The impact of limited oxygen on the extraction of nickel and copper from the selected ore was investigated in two sets of four columns operated in series for 90 days (Figure 1), each with approximately 0.45 m depth of ore. One set of columns was aerated via a stream of air from the bottom of each column. Columns in the second set were sealed at the top and did not have air inlets at the bottom. While the unaerated columns were not completely anaerobic, it was anticipated that there would be a significant difference in the available oxygen content between the two sets of columns. In this way, it was hoped to simulate the conditions that might prevail in regions of a poorly aerated but not anaerobic, heap.

Discharge solutions from each column and the two reservoir solutions were monitored for a 90-day period. There was a distinct gradient in discharge solution pH as the synthetic leach solution percolated through the 1.8 m depth of ore for both the

aerated and unaerated tests (Figure 2A, C). Data for the aerated columns gave a clear indication of the acid front moving through the columns as a function of time, as the reactive mineral phases consumed acid (Figure 2B). The trend was evident for the unaerated columns but the data were more variable (Figure 2D). In both data sets, the highest pH recorded during the experiment was pH 4.3.

Redox potentials were strongly influenced by solution chemistry parameters that can cause changes in soluble iron speciation, in particular pH, but also iron and sulfate concentrations and ionic strength. The relationship between pH and redox potential for the solution composition used in this study is summarised in Table 3. The redox potentials of the discharge solutions showed a clear trend with depth and time for the aerated columns, tending towards 400 mV (Figure 3A) as the pH values approached pH 2 (Figure 2B). The data for the unaerated columns (Figure 3B) were more variable, as was observed for the pH data (Figure 2D).

In less than a day, the ferrous ion concentrations rose to about 2000 mg/L in the discharge solutions at 0.45 m, lessening proportionally with depth to about 800 mg/L at 1.8 m. However, this depth profile was lost by day three of leaching, when all discharge solutions had similar ferrous ion concentrations of about 2000 mg/L. Ferrous ion concentrations increased steadily as a function of time from 2000 mg/L to about 6000 (45 mg/L/d) and 8000 mg/L (65 mg/L/d) for aerated and unaerated columns, respectively. There was little difference in rates between columns within each serial-set of four columns. Total iron concentrations were not measured for the discharge solutions, but comparison with iron concentrations in reservoir solutions showed that soluble iron was almost entirely ferrous ion. This and the low redox potentials indicated that leaching was abiotic throughout this experiment.

While there was a steady increase in total iron concentrations in the two reservoirs, ferric ion concentrations dropped rapidly from the initial 660 mg/L of the column feed solution (the synthetic leach solution – Table 2) to zero and remained there for both aerated and unaerated columns (Figure 4). The absence of air made very little difference to the behaviour of iron or nickel. Nickel concentrations reached about 1000 mg/L for the aerated column and about 850 mg/L for the unaerated column in 90 days, representing about 14% and 12.5% extraction of contained nickel, respectively.

In contrast, within 30 days, 85% of the initial copper content of the column feed solutions had failed to report to reservoir solutions for both aerated and unaerated columns (Figure 5). A second charge of copper sulfate was added to each of the reservoirs on day 36 (Figure 5). The additional copper was also stripped from solution in both aerated and unaerated columns until day 55, after which copper concentrations increased and remained higher in the aerated column reservoir to the end of the experiment. This difference was attributed to the lower pH of the leach solution (Figure 2B) resulting in smaller loss of copper from solution during leachate percolation through the bed and/or the re-dissolution and downward transport of copper previously retained within the column. Continued high and variable pH in the unaerated columns (Figure 2D) was reflected in continued loss of copper from solution. Thus, while oxygen limitation did not impact greatly on the chemistry of copper loss from solution, it did play a role in subsequent copper recovery under conditions of lower pH.

The metal content throughout even a well-mixed mass of ore can vary significantly between sub-samples due the heterogeneity of the ore at the particle size range used (-6.7+4.75 mm). Representative head samples were therefore separated from each column charge prior to loading, using a riffle splitter. Elemental analysis of the samples showed differences up to 11% in mass of copper per column (Table 4). At the conclusion of the experiment, representative samples of the column residues were analysed and a mass balance for copper estimated. Within analytical error, all of the copper was accounted for in both aerated (100.4%) and unaerated (100.3%) columns. The changes in copper mass per column were small but nevertheless indicative of copper re-distribution during leaching (Table 4). For both aerated and unaerated systems, copper lost from the first column was gained by subsequent columns in each series. Greatest deposition of copper occurred in the second column (0.45-0.9 m depth) in the time frame of these experiments. In the test heap, irrigated with a more acidic solution (pH 1.4-1.8), greatest copper 'redistribution' occurred at 1-2 m depth (Table 1).

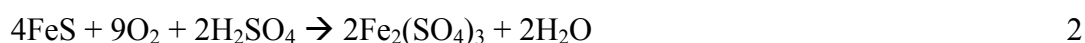
In summary, parameters monitored in column discharge solutions, pH, redox potential and ferrous ion concentration, provided insights regarding leach chemistry at intervals within the 1.8 m bed of ore. Elemental concentrations in the column reservoirs indicated the extent of nickel, copper and iron extraction and leach residue



analyses were used to estimate a copper mass balance for each column. While lack of oxygen caused more variable leach chemistry in the unaerated column series, overall, aeration had a relatively small effect leach chemistry for copper and nickel. However, the data indicated that pH played role in copper redistribution within each series of columns and that both pH and aeration played a role in subsequent copper recovery.

### 3.2 *Impact of feed solution pH on abiotic leaching*

Independently-operated, unaerated columns were used to investigate the effect of solution pH on copper behaviour. The synthetic leach solutions used in this experiment (Table 2) contained the same concentrations of nickel, copper and iron as the synthetic leach solution used for the aeration study, but the iron was added as ferrous sulfate to avoid hydrolysis reactions that could lead to *in situ* acid generation (Equation 1) (Aylward and Findlay, 1971). The oxidative leaching of sulfides in these columns was expected to be minimal, only utilising ferric ions generated by the acid dissolution of pyrrhotite, the most reactive of the sulfides in the ore (Equation 2). In oxygen depleted parts of the columns the reaction would be more likely to generate ferrous ions (Equation 3).



Total iron contents in the column reservoirs increased steadily from 6 g to between 45 g (pH 1) and 12 g (pH 2). The iron content was unchanged in the reservoir for the pH 2.5 column and decreased for columns with higher-pH feed. Ferric ion concentrations were negligible in all reservoir solutions except that of the pH 1 column, where ferric ion comprised about 10% of the total soluble iron. Nickel contents in all reservoirs increased from an initial content of 0.76 g to between 1.84 and 2.64 g in 25 days. In view of the nickel content of the pyrrhotite and chlorite, the increased nickel content during leaching is assumed to have come mainly from acid dissolution of pyrrhotite and chlorite rather than from pentlandite oxidation.

The mass of copper in each reservoir changed depending upon the pH of the feed (Figure 6) and each column discharge had a solution pH consistently higher than

its column feed, as anticipated. For the reservoir maintained at pH 1.0, the column discharge was in the range pH 1.5-1.8 for the duration of the experiment. There was a net copper gain in the reservoir, indicating that soluble copper was stable in this pH range and that some chalcopyrite leaching had taken place. The discharge solution from the pH 1.5 column ranged between pH 2.2 and 2.4 and copper loss from solution was significant. Greatest rates of copper loss from solution occurred in the columns with higher pH feed solutions.

The results were consistent with those observed for the aerated and unaerated columns run in series. For both series, the pH of the discharge solution from the first column (0.45 m) remained at about pH 2.5 following the initial rapid acid consumption by reactive minerals (Figure 2). In both these columns there was a net copper loss from the column to solution (C1, Table 4). For subsequent columns in the series, the discharge solution pH values were higher and there was a net copper gain in the column.

### 3.3. *Ancillary leaching tests*

Despite the careful set up and operation of the columns, it was not possible to control the pH of the solution as it percolated through the ore bed. The leaching of pulverised ore (4 g, 100% passing -125  $\mu\text{m}$  screen) in flask tests gave greater certainty as to the pH of the bulk solution contacting the particles. Flasks initially contained 0.012 g Cu in solutions of different pH. The flasks were agitated and aerated using an orbital shaker and the solution pH adjusted periodically.

For flasks at pH  $<2.5$ , soluble copper content increased in proportion to increased acidity. For flasks at pH  $\geq 2.5$ , soluble copper content diminished rapidly to very low levels, indicating that there was a change in the stability of soluble copper between pH 2 and 2.5 (Figure 7).

Much of the reaction occurred in the first 24 hours and trends in copper behaviour were largely established in a 96-hour period. Some copper was re-solubilised in flasks at pH  $>2.5$ , probably as a consequence of the continued acid additions to the flasks to maintain the required pH. Flasks with pH  $<2.5$  contained significant iron throughout the experiment, up to 4000 mg/L at pH 1. Due to the well-aerated conditions within the flasks it is possible that some of the ferrous ions were

oxidised and that the ferric ions then reacted with the ore and/or the copper precipitates. The acid dissolution of pyrrhotite in an oxygenated system (Equation 2) could also have contributed ferric ions which reacted with the precipitated copper species. However, significant ferric ion concentrations were only detected in the pH 1.0 flask, and in the pH 1.5 and 1.8 flasks in much smaller concentrations towards the end of the experiment.

A second experiment was carried out using an initial 1 g/L copper concentration for a 72-hour reaction period to maximise the amount of copper precipitated or adsorbed on the ore and to avoid the re-dissolution of any precipitated/adsorbed copper. Duplicate flasks, prepared without the ore, confirmed that loss of soluble copper was the result of interaction with a component of the ore and not purely a function of solution pH. While the results (not shown) corroborated the longer-term flask tests (Figure 7), the higher copper concentrations only resulted in a slightly greater mass of copper being removed from solution at a given pH. Application of the 0.33 g/L copper solution yielded approximately 0.01 g of precipitated/adsorbed copper at pH 4 after 70 hours, while for the 1 g/L copper solution only 0.013 g was removed from solution at pH 4. This result indicated that copper was interacting with a minor component of the ore.

In summary, the results of the flask tests displayed a similar relationship between copper and solution pH as those obtained from the column experiments. Copper was lost from solution rapidly at  $\text{pH} \geq 2.5$ . The smaller particle size used in the batch studies, compared with the columns, provided a larger reactive surface area with which the copper could react. The mass of copper deposited on the unreacted solids in these experiments was insufficient for the identification of an insoluble copper species.

#### **4. Discussion**

The results from this suite of column and flask tests indicated that pH played a key role in the dissolution and precipitation or adsorption of copper for the pyrrhotite-rich copper-nickel ore. Copper appeared to be stable in solution at a pH less than or equal to pH 2.3. Above this pH the copper was stripped from solution at an increasing rate with increasing pH. At  $\text{pH} > 3.8$  the soluble copper reacted rapidly to form

insoluble products or was adsorbed onto ore particles. In these tests, aeration had a minor role in copper recovery in the presence of a favourable leachate pH. It was concluded that pH impacted directly on the balance between copper recovery and copper deposition in the ore bed and that a suitable pH and aeration were needed to effectively re-leach deposited copper.

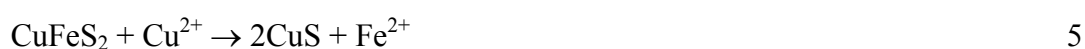
The strong influence of soil solution pH on copper adsorption on mineral surfaces is a well known phenomenon of particular interest in soil science (e.g., [Alva et al., 2004](#); [Mouta et al., 2008](#)). It has been studied for individual soil minerals such as hematite or goethite and for clay minerals such as kaolinite, illite and others ([Kinniburgh et al., 1976](#); [Benjamin and Leckie, 1981](#); [Wu et al., 1999](#)). Thus, copper adsorption onto gangue minerals in low-grade ores and/or the reaction products of gangue mineral dissolution probably contributes to copper losses from solution during heap leaching. However, adsorption is unlikely to be the sole mechanism for copper removal during heap leaching because significant delays in copper recovery, such as those reported for the copper-nickel test heap, are not usually noted for copper oxide and secondary copper sulfide heaps. In addition, copper adsorbed on gangue minerals would respond to leachates of greater acidity without the requirement for air.

The deposition of insoluble copper species on sulfide minerals is also known to occur, but usually not to the extent that was experienced in the test heap of copper-nickel sulfide ore and observed in subsequent experiments. For example, pyrrhotite, the major and most reactive sulfide mineral present in the ore, can undergo non-oxidative dissolution in acidic conditions to yield hydrogen sulfide (Equation 3) ([Belzile et al., 2004](#)). The reaction of cupric ions with hydrogen sulfide in acidic solution to form covellite (CuS) is well known (Equation 4) and covellite formation on pyrrhotite surfaces as well as in the form of discrete grains in chalcopyrite-pyrrhotite tailings has been reported ([Holmström et al., 1999](#)); in that study, a three-fold copper enrichment occurred just below the oxidation front. Secondary covellite formation has been reported for other base metals tailings ([Blowes and Jambor, 1990](#); [Lin and Herbert, 1997](#)). Similarly, [Öhlander et al. \(2007\)](#) quantified trace elements on pyrite surfaces and found that copper was enriched on pyrite from mine tailings sampled from below the oxidation front. They did not identify the copper species formed but concluded that reaction with the pyrite or adsorption onto the surfaces of

pyrite or insoluble ferric oxyhydroxides were important retention processes for copper below the oxidation front.



The reaction of copper ions directly with chalcopyrite is another mechanism by which covellite may be formed. Roman et al. (1999) found greater amounts of covellite in the leach residues than was present in the head sample of a mixed copper oxide-chalcopyrite ore, and concluded that the chalcopyrite was being transformed to covellite during leaching (Equation 5). As leaching proceeded, the covellite would be oxidised and the copper extracted (Equation 6).



For the copper-nickel ore of the present study, reaction with pyrrhotite is more likely to have occurred because the pyrrhotite had both greater exposure on particle surfaces and greater content than the chalcopyrite.

As it had appeared that the copper was being held up in the most poorly aerated regions in the copper-nickel test heap (Table 1), and that lack of aeration resulted in minimal copper recovery from a one metre column (Watling et al., 2009), it was hypothesised that a lack of available oxygen/air in these regions of the test heap was responsible for the phenomenon. Under such conditions, the bacteria present in the heap would be unlikely to assist significantly in the dissolution of the secondary sulfides as a lack of oxygen is known to greatly reduce their activity (du Plessis et al., 2001). Further, the proprietary culture used to inoculate the test heap consisted mainly of sulfur oxidizing organisms (Hunter et al., 2007), with the consequence that ferric ion concentrations in the leachates would be low throughout the heap and chalcopyrite oxidation would be minimal. It has also been reported recently that sulfate reducing bacteria (anaerobes) are able to promote the formation of covellite from acidic copper sulfate solutions (Gramp et al., 2006), another possible cause of copper hold up in the heap. However, while the absence of aeration caused more variable leach chemistry, it had only a small impact on copper extraction in the experimental columns in association with a favourable pH environment (Figure 5). Thus, overall, it is concluded that contributions to copper retention by the ore via bacterially-assisted mechanisms are minimal.

The results obtained in this study demonstrate the importance of acid management in bacterial and non-bacterial copper heap leach operations, not just in relation to the actual leaching process but the recovery of the dissolved copper from the heap itself. When ores containing large amounts of pyrrhotite or other acid-consuming minerals are present in a heap leach, it is likely that the pH within the heap will rise rapidly to levels where copper will be deposited (precipitated or adsorbed). The problem in areas of low acidity would be exacerbated by the fact that native or introduced bacteria in the heap would be less active at pH levels  $>2.5$ . As a consequence, bacterially-assisted dissolution of the precipitated copper, or of the copper sulfide in the ore, would be limited.

In order to avoid the deposition of copper becoming a significant problem within a sulfide bacterial heap leach operation, it is advantageous to ensure that the solution pH remains below pH 2.5 throughout the heap. Careful monitoring of effluent solutions from the heap would be required to ensure that heap acidity is managed appropriately. It is possible that the use of a more acid during agglomeration and stacking of the ore could assist in neutralising a greater part of the rapidly acid-consuming material before heap irrigation is commenced, thereby avoiding a large increase in leach solution pH whilst the heap is operating. It would also be advantageous to maintain the pH within the heap at as low a pH level as is conducive to bacterial growth to maximise copper recovery without undue gangue dissolution.

## **5. Conclusions**

Acidity plays a key role in maximising copper recovery from a bed of pyrrhotite-rich copper-nickel sulfide ore. When the leachate pH rises to  $>2.3$ , copper ions are retained by adsorption on, or reaction with, ore minerals. Air limitation had only a small impact on copper recovery in this study, in association with a favourable pH environment. Possible reaction mechanisms for copper retention are discussed but the amounts of copper being retained within the ore were too low to allow corroboration of the mechanism(s) using instrumental methods of analysis. The results indicate the need for careful acid management in the operation of heaps of pyrrhotite-rich ores such as complex copper-nickel sulfide ores.

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Table 1. Non-chalcopyrite copper determined by selective leaching of test heap samples as a percentage of the total copper

Head	Post-leach samples at depth			
	surface	0-1 m	1-2 m	2-3 m
4.67	12.5	10.4	28.1	20.3

Table 2. Composition of synthetic leach solutions (pH 1.8) for abiotic column leaching experiments.

<b>Compound</b>	<b>Concentration (g/L)</b>
<b>Impact of oxygen depletion (section 2.3)</b>	
NiSO <sub>4</sub> .6H <sub>2</sub> O	0.425
CuSO <sub>4</sub> .5H <sub>2</sub> O	0.330
FeSO <sub>4</sub> .7H <sub>2</sub> O	0.006
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .9H <sub>2</sub> O *	3.110
Sodium Benzoate (CH <sub>3</sub> COONa)	0.100
<b>Impact of pH (section 2.4)</b>	
NiSO <sub>4</sub> .6H <sub>2</sub> O	0.425
CuSO <sub>4</sub> .5H <sub>2</sub> O	0.330
FeSO <sub>4</sub> .7H <sub>2</sub> O	3.730
Sodium Benzoate (CH <sub>3</sub> COONa)	0.100

\* water of hydration determined by drying at 50°C for 48 h.

Table 3. Relationship between pH and redox potential for the synthetic leach solution used as column feed for the aeration experiments.

pH	1.0	1.5	1.8	2.0	2.5	3.0	4.0	5.0
Redox (mV vs Ag/AgCl)	529	529	527	519	515	500	483	448

Table 4. Redistribution of copper in the leach residues from the unaerated and aerated columns.

	Copper (g)					
	C 1	C 2	C 3	C 4	Solution	Series
Aerated columns						
Initial	62.07	57.33	59.66	61.07	1.45	241.59
Added					1.61	243.20
End	54.60	62.88	63.93	61.83	0.85	244.09
Change	-7.47	+5.55	+4.27	+0.76	-2.21	
Unaerated columns						
Initial	66.78	60.42	59.36	63.89	1.47	251.92
Added					1.47	253.39
End	62.73	64.42	61.01	66.00	0.07	254.22
Change	-4.05	+4.00	+1.65	+2.11	-1.4	

## Figure captions

Figure 1. Schematic diagram showing the flow of synthetic leach solution and air through four columns operated in series. The four unaerated columns were set up without air inlets.

Figure 2. Discharge solution pH as a function of time: A & B, aerated and C & D, unaerated. ♦ 5 days; ■ 20 days; ▲ 50 days; □ 65 days; △ 85 days;

Figure 3. Redox potential of column discharge solutions: A, aerated and B, unaerated.

Figure 4. Nickel, total iron and ferric ion concentrations in column reservoir solutions.

Figure 5. Copper concentrations in reservoir solutions for aerated and unaerated columns.

Figure 6. Mass of copper in column reservoirs maintained in the pH range 1.0 to 4.0.

Figure 7. Mass of copper in leachates for flasks that contained 4 g pulverised ore and 0.012 g Cu as copper sulfate. The legend denotes the initial solution pH.

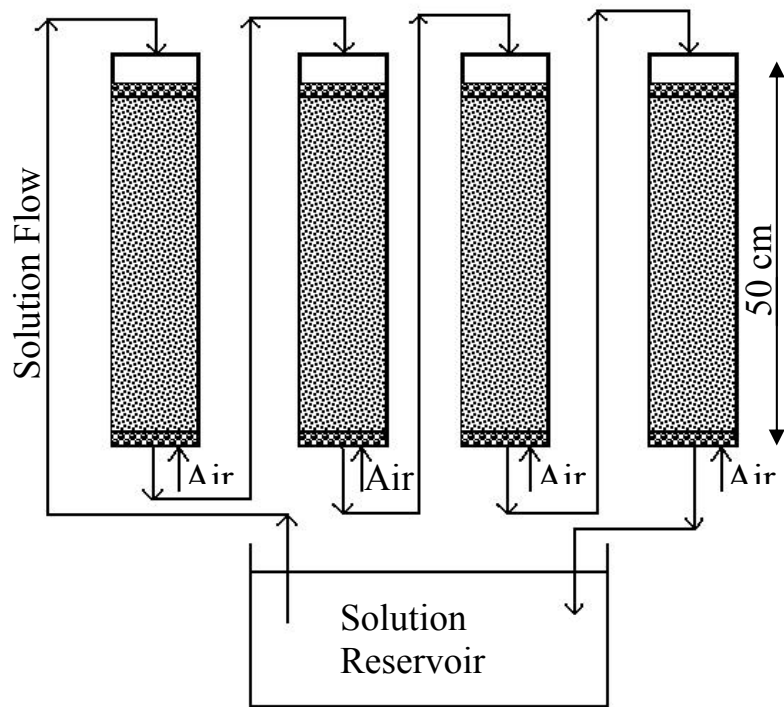


Figure 1. Schematic diagram showing the flow of synthetic leach solution and air through four columns operated in series. The four unaerated columns were set up without air inlets.

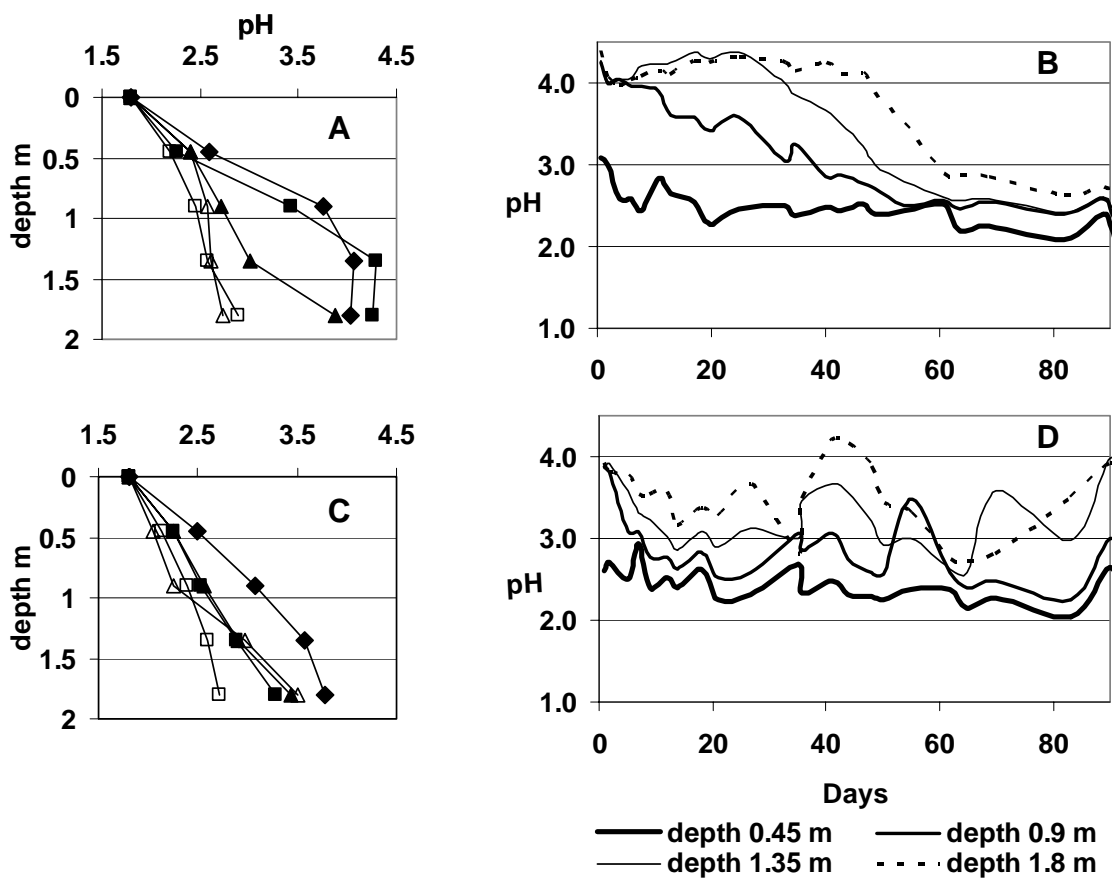


Figure 2. Discharge solution pH as a function of time: A & B, aerated; C & D, unaerated. ◆ 5 days; ■ 20 days; ▲ 50 days; □ 65 days; △ 85 days;



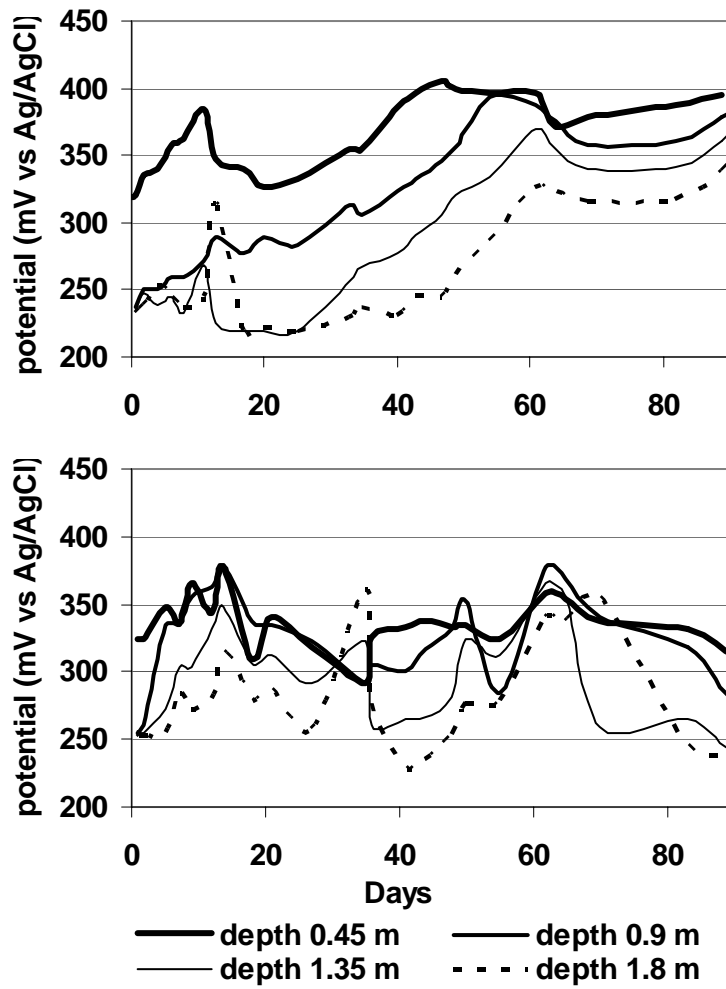


Figure 3. Redox potential of column discharge solutions: A, aerated and B, un-aerated

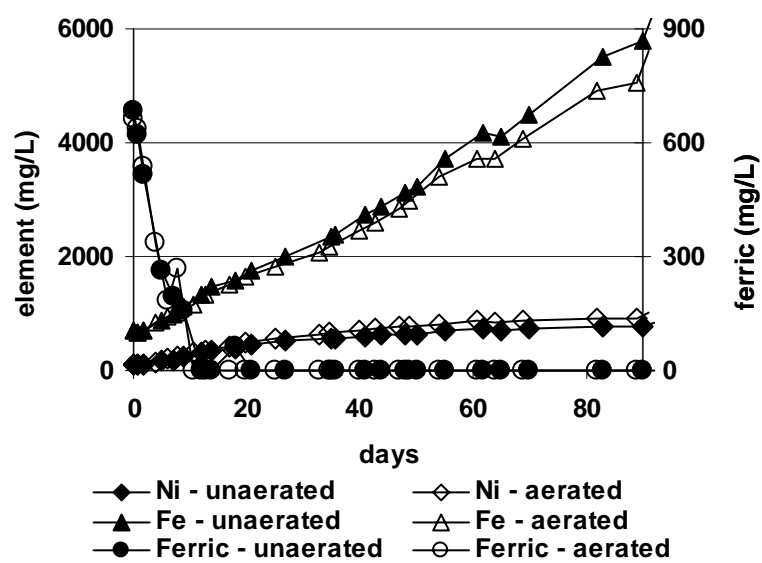


Figure 4. Nickel, total iron and ferric ion concentrations in column reservoir solutions.

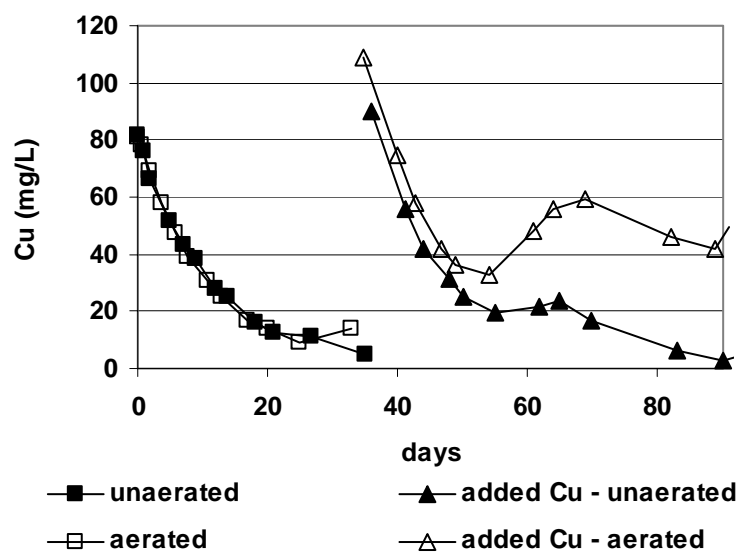


Figure 5. Copper concentrations in reservoir solutions for aerated and un-aerated columns.

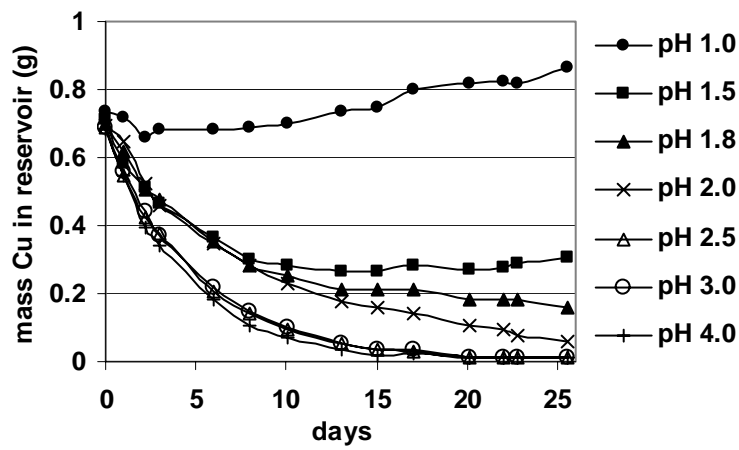


Figure 6. Mass of copper in column reservoirs maintained in the pH range 1.0 to 4.0.

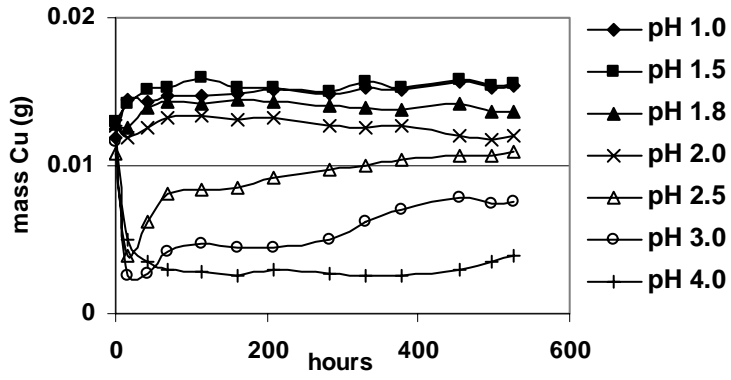


Figure 7. Mass of copper in leachates for flasks that contained 4 g pulverised ore and 0.012 g Cu as copper sulfate. The legend denotes the initial solution pH.