

# Pressure oxidation leaching of chalcopyrite. Part I. Comparison of high and low temperature reaction kinetics and products

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## Abstract

The kinetics and products from the pressure oxidation of a chalcopyrite concentrate are compared under a range of reaction conditions promoted by various companies. The reaction conditions compared in this article, Part I, are referred to as the Phelps Dodge-Placer Dome and Activox<sup>®</sup> processes. The medium temperature processing of the concentrate will be reported in Part II.

Experiments were conducted with the same concentrate over a temperature range of 108–220 °C with different salt and acid additions to compare the kinetics and recovery of copper, the speciation of sulfur and the deportment of iron-containing and other phases in the leach residues. The aim was to improve understanding of the mechanism and practical issues for the competing processes and to provide background knowledge often not available in the public domain.

The chalcopyrite concentrate was found by Quantitative X-ray Diffraction (QXRD) analysis to contain about 80% chalcopyrite, 10% quartz, 6% pyrite and 2.5% talc and 1.5% clinocllore. It was demonstrated that greater than 94% of the copper could be extracted from the concentrate using either the Phelps Dodge-Placer Dome or Activox<sup>®</sup> process within 30 min. The extraction of the residual copper was strongly influenced by the presence of elemental sulfur.

About 80–90% oxidation of sulfide to elemental sulfur occurred at 108 °C and was enhanced by the presence of the chloride ion. Above 180 °C there was complete oxidation to sulfate. However, in the presence of added chloride ion the rate of sulfate formation decreased.

QXRD was employed to examine the leach residues. Iron was leached and re-precipitated forming a number of different phases depending upon the process temperature, acidity and salinity. At low temperature, in the presence of chloride, akaganéite was formed together with an uncharacterised amorphous hydrated iron oxide. Hematite formation was favoured at temperatures  $\geq 150$  °C, low acidity and low salinity; basic ferric sulfate formed at high temperature (220 °C), high acidity and low salinity. Goethite formation was favoured at  $\leq 150$  °C by low acidity and low salinity. Jarosite was formed at all temperatures under conditions of moderate to high acidity and its formation was enhanced in the presence of sodium ions.

Several basic copper salts including atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) and antlerite ( $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ ) were precipitated at 108 °C at low acidity, typically at pH > 2.8. Atacamite formed initially when the sulfate concentration was low but dissolved and the copper was re-precipitated to form antlerite as the sulfate (and copper) concentrations increased.

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## 1. Introduction

High temperature (200–230 °C) acid pressure oxidation leaching of metal sulfides was first commercialized

in the 1950's. However, the more recent commercial success of medium temperature pressure oxidation of zinc sulfide concentrates and high temperature pressure oxidation of refractory gold ores and concentrates has contributed to renewed interest in the total oxidative leaching of copper sulfides, especially chalcopyrite. An early overview of the role of pressure oxidation in treating refractory gold ores was given by [Berezowsky and Weir \(1989\)](#) while subsequent developments are highlighted by [Sinadinović et al. \(2001\)](#) and include the PLATSOL process ([Ferron et al., 2002](#); [Dreisinger et al., 2005](#)). Examples of pressure oxidation plants commissioned since the mid-1980's and a brief description of their operation can be found in the article by [Mason and Gulyas \(1999\)](#).

Historically copper sulfides have been smelted, however, since the early 1990's a number of prospective leaching processes have been successfully demonstrated at the pilot plant scale. An excellent review describing these and related processes is given by [Berezowsky and Trytten \(2002\)](#) while recent discussions of the hydrometallurgical processes for treating copper concentrates have been presented by [Dreisinger \(2004, 2006\)](#). Commercially such treatments were until recently restricted to operations such as the Mt Gordon pressure oxidation/ferric leaching plant ([Dreisinger et al., 2002](#)) and Oxiana's Sepon project ([Baxter et al., 2004](#); [Keokhounsey et al., 2006](#)), both of which treat chalcocite-containing feeds.

Nowadays the commercial leaching of chalcopyrite is also a reality. Phelps Dodge has employed high temperature pressure oxidation, albeit at pilot scale, since 2003 for the processing of chalcopyrite concentrate at the Bagdad mine in Arizona. The start-up, operation and optimization of this facility were reported by [Wilmot et al. \(2004\)](#). Recently, in June 2005, the same company announced plans to build the a commercial-scale copper concentrate facility at the Morenci Mine with a projected output of 235 kt or copper per annum. The facility will employ proprietary technology captured by the invention of [Marsden et al. \(2005\)](#).

The hydrometallurgical processes that have been developed for the pressure leaching of chalcopyrite can be classified into low, medium and high temperature regimes. Low temperature processes employ ultra-fine grinding to enhance the leaching kinetics and give high conversions of sulfide to elemental sulfur. Medium temperature processes utilize fine grinding, higher temperatures, typically 140–150 °C, but require the addition of specific reagents to minimise wetting of the chalcopyrite surface by molten sulfur that would otherwise slow the leaching kinetics. Again, moderate to high

conversions of sulfide to sulfur can be obtained and the leach residues are generally quite stable, having low sulfate content. At high temperatures, 200–230 °C, leaching kinetics are rapid, however, the entire sulfide content is converted to sulfate leading to substantially higher oxygen consumption and producing higher free acid levels. The adoption of such processes has been slow due to the economic strength of the smelting process, that includes heavy capital investment, the availability of markets for sulfuric acid, until recently, few environmental pressures to minimise sulfur dioxide output, the recovery of energy from smelter gases and a lower electricity requirement for the electrowinning of blister copper than hydrometallurgical processes require for copper electrowinning. Factors that would tend to favour hydrometallurgical treatment include location near to a mine site, a nearby source of process water, for the processing of "dirty" concentrates, the use of acid by-product for heap bioleaching or the leaching of oxide ores, and for the conversion of an existing plant from the treatment of oxide to sulfide ores. Other key factors to the selection of a sulfide leach process have been discussed in detail elsewhere ([Jansen and Taylor, 2000](#)) while the commercial drivers for the application of a high temperature pressure leach process to copper concentrates are discussed by [Marsden et al. \(2003\)](#).

A number of distinctly different processes have been developed and patented by various commercial companies which give limited disclosure of the technical knowledge. One of these, referred to as the Phelps Dodge-Placer Dome process, was the first to be commercially applied to the processing of chalcopyrite concentrate at the Bagdad mine. Other prominent methodologies available include the Anglo American Company-University of British Columbia (Anglo/UBC), Cominco Engineering Services Limited (CESL), Dynatec, nitrogen-species catalyzed (NSC) and Activox® processes. The primary aims of this study were to:

- Compare the effectiveness of the various processes in terms of leaching kinetics and reagent consumption, with the same ore sample.
- Determine the effects of changing process water salinity and chloride ion upon the kinetics, mechanism and products of reaction.
- Characterise and quantify the materials present in the leach residue.

Part I of this work compares the results of tests conducted at high temperature, with total sulfur oxidation; and at low temperature, below the melting point of sulfur, with little sulfur oxidation. Subsequently, Part II

will compare test work conducted at medium temperature, where sulfur is molten, with a variety of additives designed to disperse the sulfur and enhance copper recovery.

## 2. Experimental

A chalcopyrite concentrate (as-received) was lightly ground and dry screened to produce  $-106, +75 \mu\text{m}$  and  $-45 \mu\text{m}$  size fractions. Ultra-fine milling of the as-received material to  $-10 \mu\text{m}$  was performed using a ceramic ball mill and confirmed by particle size analysis.

All experiments were conducted using a Parr 1 gal. (U.S.) 4551 M model vertical reactor constructed from Grade 3 titanium and controlled to within  $\pm 2^\circ\text{C}$  using a Parr 4842 model temperature controller. Agitation at speeds of 1000 rpm was provided by a magnetically driven twin impeller. Typically the vessel was loaded with 10% or 20% w/w pulp density slurry of chalcopyrite concentrate with various lixiviants, depending upon the chosen extraction process. A summary of the experimental conditions is given in Table 1.

The system was then heated under a blanket of nitrogen to the required temperature, oxygen injected on a continuous basis to maintain the target oxygen partial pressure and the reaction continued for periods varying between 90 and 240 min.

Samples taken at regular intervals were filtered through  $0.45 \mu\text{m}$  membranes, the primary filtrate collected and the solution density determined. The solids were washed thoroughly with de-ionised water, dried overnight at  $70^\circ\text{C}$  and lightly ground. Both the liquor and solid samples were submitted for analysis by ICP-AES for the

elements Cu, Fe, S, Si, Mg, Al, Ca and Na. The residues were analyzed after fusion at  $900\text{--}1000^\circ\text{C}$  with the Sigma Chemicals 12:22 lithium borate flux and dissolution. When elemental sulfur was present in the residue, sulfur analyses were performed using a LabFit CS-2000 analyzer with electrical furnace heated to  $1400^\circ\text{C}$ .

The acidity of the filtrate samples was determined after dilution, adjustment of the Eh to  $>600 \text{ mV}$  with  $\text{Na}_2\text{S}_2\text{O}_8$  solution, addition of a 20% excess of calcium EDTA solution and titration with sodium hydroxide to an endpoint pH of 5.7.

Solid sub-samples were weighed with the addition of 10% fluorite (internal standard) and lightly milled using either a SPEX 8000 ball mill or a McCrone micronizing mill prior to submission for XRD measurement. XRD traces of the ground samples were obtained on a Philips Xpert diffractometer, using the following acquisition conditions: Co  $\text{K}\alpha$  radiation,  $5\text{--}120^\circ 2\theta$  Co  $\text{K}\alpha$ ,  $0.05^\circ 2\theta/\text{step}$ ,  $1.5^\circ 2\theta/\text{min}$ , primary and secondary Soller slits installed (receiving slit  $0.2 \text{ mm}$ ). Rietveld refinements were conducted using KoalaRiet software and a verified set of crystal structures.

## 3. Ore characterisation

Quantitative X-ray Diffraction (QXRD) analysis of the concentrate employed in the present study indicates that the material consists of 79.8% chalcopyrite ( $\text{CuFeS}_2$ ), 10.0% quartz ( $\text{SiO}_2$ ), 5.9% pyrite ( $\text{FeS}_2$ ), 2.4% talc ( $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ ), 1.4% clinocllore (e.g.  $(\text{Mg,Fe})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$ ) and a trace, ca 0.5%, of elemental sulfur. The calculated elemental analysis based upon QXRD was in very good agreement with chemical analysis based upon ICP-AES.

Table 1

Experimental conditions employed for Phelps Dodge-Placer Dome and Activox® leaching experiments from the present study

Temp. ( $^\circ\text{C}$ )	$\text{P}(\text{O}_2)$ (kPa)	Leach time (min.)	Solids loading (% w/w)	Nominal particle Size ( $\mu\text{m}$ )	$P_{80}$ ( $\mu\text{m}$ ) <sup>a</sup>	Lixiviant with Cl (as NaCl)
<i>Phelps Dodge-Placer Dome</i>						
220	700	90	10	−45	N/D	5 g/L $\text{H}_2\text{SO}_4$
200	700	90	10	−45	N/D	5 g/L $\text{H}_2\text{SO}_4$
190	700	90	10	−45	28.2	Water only
180	700	90	10	−45	28.0	Water only
220	700	90	10	−106, +75	N/D	5 g/L $\text{H}_2\text{SO}_4$
220	700	90	20	−45	N/D	5 g/L $\text{H}_2\text{SO}_4$
220	700	90	20	−45	N/D	10 g/L Na
<i>Activox®</i>						
108	700	240	10	−10	8.0	10 g/L Cl
108	700	180	10	−10	11.2	3 g/L Cu, 5 g/L $\text{H}_2\text{SO}_4$
108	700	180	10	−10	7.2	3 g/L Cu, 10 g/L Cl, 5 g/L $\text{H}_2\text{SO}_4$
108	700	180	10	−10	9.7	3 g/L Cu, Fe; 20 g/L Cl, 50 g/L $\text{H}_2\text{SO}_4$

<sup>a</sup> N/D=Not determined.

#### 4. High temperature oxidation

##### 4.1. Development of the Phelps Dodge-Placer Dome and related total POX processes

A summary of early developments in the high temperature oxidation of refractory gold ores and concentrates, where the gold is usually locked up in pyrite and arsenopyrite, and including references to the Sherritt test work that took place in the 1980's, has been presented by Berezowsky and Weir (1989). Placer Dome in conjunction with the University of British Columbia in the early 1990's also evaluated several chalcopryite concentrates by high temperature leaching followed by the cyanidation of the leach residues for gold recovery. All concentrates responded well to leaching at 200–220 °C with copper extractions of 98% or higher and noxious impurities such as Sb, As, Bi, Se and Te primarily reported to the leach residue; the deportment of Hg was found to vary with a significant amount reporting to the leach liquor (King et al., 1993; King and Dreisinger, 1995).

As a result of early studies on refractory gold concentrates, pressure oxidation circuits were commissioned by Placer Dome at the Porgera and Campbell mine sites and both are still operating today. A pressure oxidation circuit was also operated at the Getchell property (*aka* Turquoise Ridge JV), however, components of this facility were sold and demobilized in 2005.

Other gold producers have employed pressure oxidation technology to oxidise gold-bearing pyrite. Refractory ore from Barrick Gold's Goldstrike property is currently pre-treated in an autoclave whilst ore from the Mercur mine, now decommissioned and closed, was also processed under alkaline oxidation conditions. Despite concentrate from Barrick's El Indio mine having been successfully treated at the bench scale, no scale-up occurred. Newmont operate autoclaves at both the Twin Creeks and Lone Tree operations in Nevada, and Lihir Gold treat their refractory ore at 210 °C (Collins et al., 1993). Although the installation of a pressure oxidation circuit at the Homestake McLaughlin operation was the first of its kind, both mining and use of the autoclave ceased in 1997.

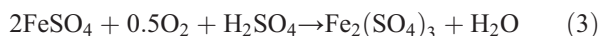
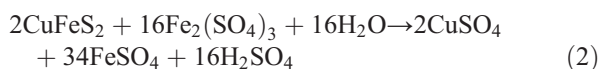
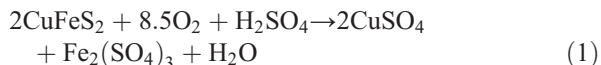
The pressure oxidation facility from the Getchell property was purchased by First Quantum Minerals for the oxidation a gold-bearing copper ore at the Kansanshi operation. It was due to be commissioned in the final quarter of 2006. The leach circuit is designed to operate at 210 °C with a residence time of 1.7 h (Dunn, 2006). Pressure oxidation has also been evaluated for the Guelb Moghrein copper–gold deposit but was abandoned to

develop facilities for the production of a copper–gold concentrate. Concentrate from the Konkola deposit (owned by Konkola Copper Mines plc) was also shown to leach well at 200 °C, however, conventional processing techniques are still being employed.

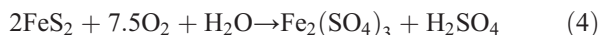
The use of total pressure oxidation for the treatment of chalcopryite concentrates by Phelps Dodge dates back to 1999 and following continuous testing, Phelps Dodge and Placer Dome entered into a Technology Development Agreement related to further development, commercialization, use and potential licensing of the technology to other parties (Marsden et al., 2003). Subsequently, Phelps Dodge proceeded with the design and construction of a commercial-scale pressure oxidation plant that commenced operation at the Bagdad site in March 2003. This plant was rapidly commissioned and operated above the design capacity of 15,700 tpa copper cathode throughout the remainder of that year (Wilmot et al., 2004). In comparison with proposed conditions for the Kansanshi operation, a higher temperature of 225 °C and shorter residence time of 60–65 min are employed (Marsden et al., 2003).

##### 4.2. Chemistry

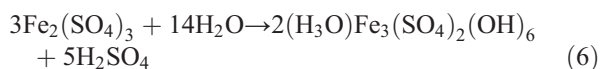
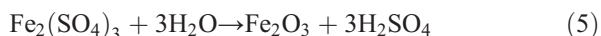
The reaction of chalcopryite (and pyrite) at high temperature (180–230 °C) converts sulfide sulfur entirely to sulfate and proceeds via typical reactions:



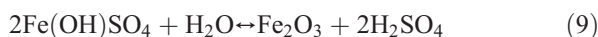
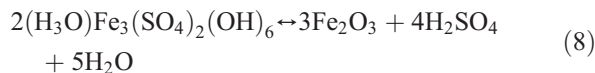
For pyrite, similar equations can be formulated with direct oxidation given as:



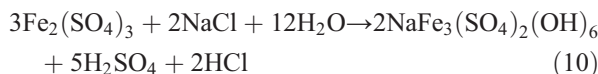
The majority of the ferric sulfate is hydrolysed at these temperatures to form hematite, hydronium jarosite or basic ferric sulfate depending upon the free acidity according to the following reactions:



The inter-conversion of iron-containing residues at low acidities is given by:



When monovalent alkali cations are present jarosite analogues may form via reactions such as:



Similar reactions with  $\text{Ag}^+$ , lock up silver in the residue as silver jarosite.

### 4.3. High temperature results

#### 4.3.1. Effect of temperature

The extraction of copper from a chalcopyrite concentrate (10% w/w pulp) at high temperature (180–220 °C) is shown in Fig. 1. At the highest temperature the leaching was extremely rapid and over 98% extraction was obtained in under 10 min whereas only 90% copper extraction was obtained after 2 h at 180 °C. Rapid extraction of chalcopyrite concentrate at temperatures of between 215–230 °C, pulp density of 10% and oxygen over-pressure of 700 kPa or greater was also noted during the pilot plant testing for the Bagdad operation (Marsden et al., 2003). The slower extraction kinetics with decreasing temperature has been noted by others (e.g. King et al., 1993; King and Dreisinger, 1995; Marsden et al., 2003) and also correlates with the increasing viscosity of molten sulfur in this temperature

range as the temperature decreases (Papangelakis, 2005).

The formation of soluble sulfur species (*viz.* sulfate) shows trends similar to the copper extraction but with the final sulfate extraction consistently being somewhat lower. This was in part due to the formation of crystalline sulfur-containing phases in the leach residues, including elemental sulfur, hydronium jarosite and basic ferric sulfate. However, the presence of 1.8% sulfur in the residue produced at 220 °C, for example, does not appear to be associated with any XRD-detectable phases. Examination of the sulfate to copper molar ratio indicated that when the extraction of copper and formation of sulfate were highest, the S:Cu mole ratio was about 2.25, due to the presence of pyrite in the chalcopyrite concentrate. The formation of soluble sulfate relative to the release of copper was also slower as the temperature decreased; and the lag time until the sulfate to copper molar ratio stabilises was noted to increase. This lag corresponds with a slowing rate of pyrite oxidation as the temperature decreases.

Residual copper levels of up to 0.5% were found in the final residues when the reaction temperature was 200 °C or greater. However, as there was no residual chalcopyrite detected by XRD, it is possible that a small amount of copper was adsorbed onto and/or incorporated into, the hematite that formed. Future studies will investigate using SEM-based techniques whether this is the case. A treatment process for the extraction of copper from hematite residue has been patented (Stanley et al., 1982).

According to the chemistry of the system, the solubilisation of sulfur is primarily represented as the species  $\text{CuSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{H}_2\text{SO}_4$ . In particular, the formation of free acid also follows the same trends as the extraction of copper (Fig. 2). The expected sulfate mass balance is given by the following equation:

$$[\text{SO}_4^{2-}]_{\text{TOTAL}} = [\text{CuSO}_4] + 1.5^*[\text{Fe}_2(\text{SO}_4)_3] + [\text{H}_2\text{SO}_4] \quad (11)$$

The free acid concentrations calculated according to Eq. (11) were found to be in excellent agreement, and within 2–3 g/L, of those determined by titration. The maximum free acidities were encountered at 200 °C and higher whereas at lower temperatures, where extraction was less and conversion of sulfide to sulfate was slower, the final free acidities were also lower.

The extraction of iron at high temperatures (and in the absence of chloride ions) was not significant with the bulk of the iron being precipitated as hematite. Also, as noted by previous investigators (e.g. Tozawa and Sasaki, 1986), the residual dissolved iron level

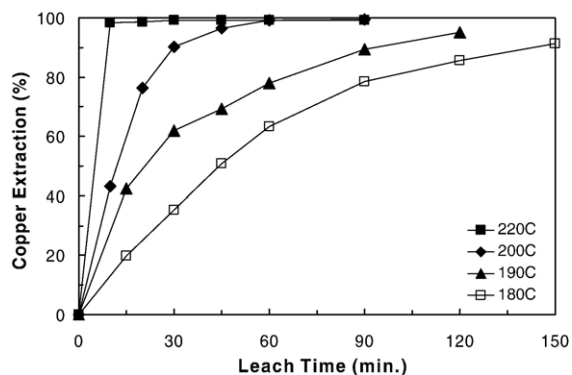


Fig. 1. Copper extraction from a 10% w/w chalcopyrite concentrate slurry using  $\text{P}(\text{O}_2)$  of 700 kPa at temperatures between 180 °C and 220 °C.



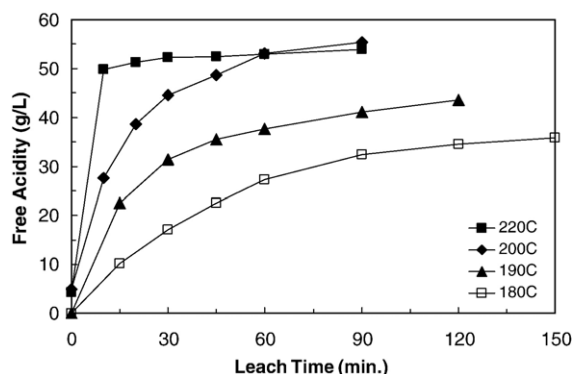


Fig. 2. Free acidity of leach liquor from a 10% w/w chalcopyrite concentrate slurry using  $P(O_2)$  of 700 kPa at temperatures between 180 °C and 220 °C. Note that the initial sulfuric acid addition was 5 g/L (220 °C and 200 °C) or none (190 °C and 180 °C).

decreases with temperature. In the present study the levels dropped from *ca* 1.5 g/L to *ca* 0.6 g/L between 180 °C and 220 °C, corresponding to iron extractions of 6% decreasing to 2%, respectively.

#### 4.3.2. Effects of pulp density, salinity and particle size

Increasing the pulp density from 10 to 20% w/w caused the initial rate of reaction to decrease (Fig. 3). Presumably this was due to the reaction becoming rate-limited by oxygen transfer into the liquor. However, copper extraction still exceeded 98% in less than 45 min, but the conversion of sulfide sulfur to sulfuric acid decreased from 96% to 85% when the pulp density was increased from 10 to 20% w/w. This result is consistent with the findings of Sinadinović *et al.* (2001) in the investigation of copper and zinc extractions from a Cu–Zn–Pb gold-bearing sulfide ore. Current mineralogical data indicate that this is due to the formation of hydronium jarosite at the higher pulp density (Section 6.1).

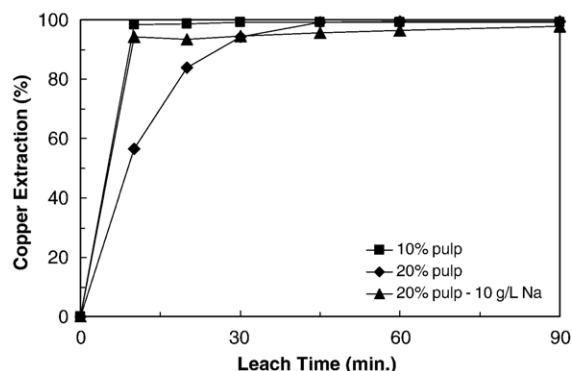


Fig. 3. Copper extractions from 10% and 20% chalcopyrite concentrate slurries using  $P(O_2)$  of 700 kPa at 220 °C, with and without added sodium chloride.

When 15 g/L chloride was added as sodium chloride the initial rate of extraction was greatly enhanced. The extraction of copper after 10 min was 94% compared with 56% in the absence of sodium chloride (Fig. 3).

Despite the rapid initial reaction rate, the final copper extraction with added sodium chloride was suppressed relative to that obtained with a 10% w/w pulp density feed. The extent of suppression decreased between 10 and 90 min and indicated the slow release of residual copper into solution. The form of the residual copper is unclear as the presence of chalcopyrite was barely detectable in the XRD pattern after 20 min (see Section 6.1). The XRD data also indicated the formation of significant amounts of elemental sulfur which may be responsible for the slowing of the reaction kinetics after 10 min. Further investigation is required to determine if this is the case. The sulfur appears to oxidise slowly to sulfuric acid even at 220 °C producing a slow increase in the concentration of sulfate after a rapid initial increase (Fig. 4), and a near linear change in free acidity (Fig. 5).

The maximum free acidities for 10% w/w and 20% w/w pulp densities were *ca.* 55 g/L and 95 g/L sulfuric acid, respectively (see Figs. 2 and 5). The former value is, not surprisingly, similar to that proposed for the Bagdad plant with a 10% w/w pulp feed (Marsden *et al.*, 2003) though it should be noted that the sulfide content of the Bagdad concentrate is marginally higher than in the present study. Increasing the pulp density and the addition of sodium enhanced the formation of sulfate-containing residues that include basic ferric sulfate and/or hydronium (or sodium) jarosite (see Section 6.1). Therefore, despite a doubling in pulp density from 10% to 20%, the free acidity did not quite double in magnitude.

At 220 °C, the extraction of iron to the leach solution was greater at higher pulp density. In addition, the iron concentration increased from 1.5 g/L to 4.8 g/L between

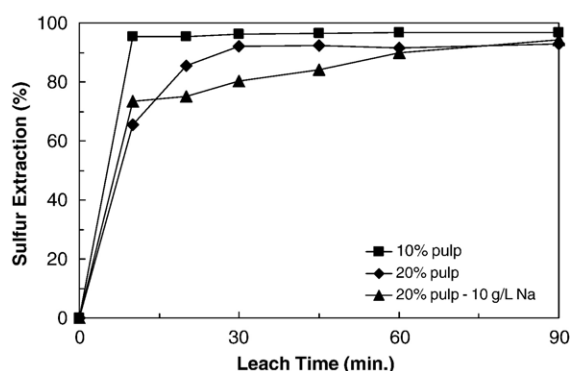


Fig. 4. Sulfur extractions (as sulfate) from 10% and 20% chalcopyrite concentrate slurries using  $P(O_2)$  of 700 kPa at 220 °C, with and without added sodium chloride.

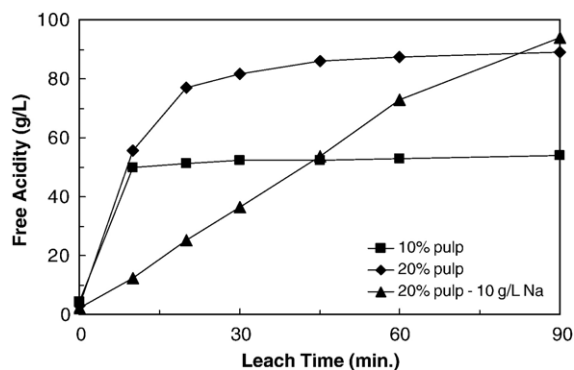


Fig. 5. Free acidity of leach liquor from 10% and 20% w/w chalcopyrite concentrate slurries using  $P(O_2)$  of 700 kPa at 220 °C with and without added sodium chloride. Note that the initial sulfuric acid addition was 5 g/L.

pulp densities of 10% and 20%, respectively. The former concentration is similar to that for the Bagdad plant (Marsden et al., 2003) indicating that sufficient oxygen was available to reaction to ensure satisfactory oxidation of ferrous to ferric iron. The greater extraction of iron at higher pulp density corresponded with the higher free acidity, a fact noted by other previous investigators (e.g. Tozawa and Sasaki, 1986). Under saline conditions the extraction of iron increased slowly during the reaction, consistent with the slower increase in free acidity (Fig. 5). However, when compared with non-saline conditions the final iron tenors were similar.

An increase in the particle size of the feed from  $P_{100}$  of 45  $\mu\text{m}$  to one of  $-106, +75 \mu\text{m}$  had only a minimal effect at 220 °C and extraction was complete after 20 min rather than 10 min.

#### 4.3.3. Sulfur oxidation

The effect of increasing chloride content on the conversion of sulfide to sulfate during pressure oxidation at lower temperatures has been documented by Subramanian and Ferrajuolo (1976) and, Stanley and Subramanian (1977), although a number of the CESL publications (e.g. Jones, 1997; Jones and Moore, 2002) extensively discuss the suppression of sulfur oxidation. In contrast, the suppression of sulfur oxidation at high temperatures is normally only mentioned in discussing the access to gold after the pressure oxidation of refractory gold concentrates in the presence of chloride ions (e.g. Collins et al., 1993; Nicol and Liu, 2003). For solids produced from tests conducted at 190 °C, optical microscopy identified elemental sulfur and when chloride concentrations were high, partially rounded droplets, a film on larger pyrite grains, and free pyrite particles attached to droplets were found (Collins et al., 1993). Increasing the oxidation temperature to 210 °C

increased the extent of sulfide sulfur oxidation, increasing the subsequent gold recovery.

The conversion of sulfide to elemental sulfur at 220 °C in the presence of added sodium chloride was determined using the analytical and QXRD data and the results compared with no sodium chloride addition in Fig. 6. The data indicate that the conversion of sulfide to sulfur was 50% under saline conditions after 10 min, whereas without any addition, no sulfur was detected. The data also indicate a nearly linear rate of elemental sulfur oxidation until, by the conclusion of the reaction, only a trace amount remained. In comparison, Nicol and Liu (2003) reported only final sulfur compositions (for a Lihir pyritic concentrate) noting the formation of over 4% elemental sulfur in the leach residue even after oxidation of a 35% solids slurry at 200 °C for 6 h in the presence of 2 M sodium chloride, and with the system maintained at a total pressure of 2000 kPa.

Increasing the sodium chloride concentration has been reported to decrease the oxidation rate of elemental sulfur at 200 °C (Corridou and Kikindai, 1981). However, this in itself is unlikely to explain the present observation. It seems more probable that the presence of chloride favours the formation of sulfur as an intermediate. Further work is required to understand the effects of sodium chloride addition.

In the absence of chloride, small amounts of sulfur were also produced during the reactions conducted at 180 °C and 190 °C but these traces were rapidly oxidised.

## 5. Low temperature processes

### 5.1. Development of the Activox® process

The low temperature processes encompass those for which the temperature is below or just above the melting

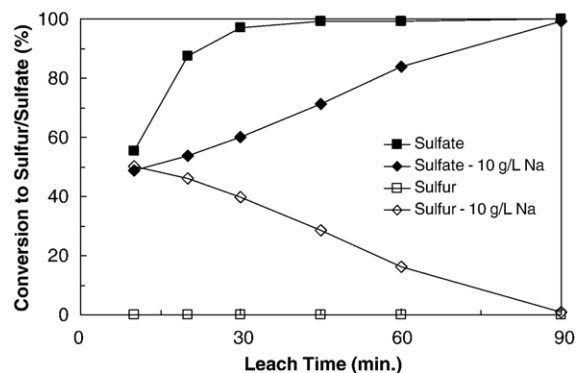


Fig. 6. Conversion (%) of sulfide to sulfur and sulfate for 20% w/w chalcopyrite concentrate slurry using  $P(O_2)$  of 700 kPa, with and without added sodium chloride.

point of sulfur. Leaching kinetics are slow below the melting point of sulfur due to the formation of a passivating layer of metal-deficient polysulfide and/or elemental sulfur. Efforts to develop a suitable low temperature process have focused upon ways of activating the chalcopryrite surface and enhancement of the leach.

Sheritt developed a low temperature pressure leach (110 °C) in the mid-1960's that involved using a high oxygen partial pressure, a fine grind to  $P_{99}$  of  $-44\text{ }\mu\text{m}$ , and an excess of concentrate relative to recycled acid, to promote the hydrolysis of iron (Vizsolýi et al., 1967; Mackiw et al., 1972). After leaching for 2–3 h the slurry was heated to 138 °C to agglomerate the un-reacted sulfides that were recovered by screening and flotation for recycling. Although relatively successful for high grade concentrates, with lower grades, the reaction of pyrite gave high acid and soluble iron concentrations and it was difficult to recover precious metals from the leach residues effectively.

The activation methods investigated in the 1970's involved thermal, mechanical and hydrometallurgical pre-treatment processes. Of these, the most relevant to current technology was mechanical activation involving ultra-fine grinding to reduce particle size, increase the surface area and produce defects in the crystal structure that might allow the material to be more readily leached. Even now, the impact of mechano-chemistry on the hydrometallurgy of sulfide ores continues to be a vibrant area of study (Baláz et al., 2005).

A discussion of the pioneering mechanical activation work by Gerlach and Pawlek is presented by Bere-zowsky and Trytten (2002). An intense milling regime was adopted as part of the Lurgi–Mitterberg process whereby the attrited “activated” concentrate was leached for 2 h at 115 °C under 1000–2000 kPa oxygen. At the time the high power requirements for activation made the process unattractive. However, development of a new generation of ultra-fine grinding technologies has substantially lowered the power requirements.

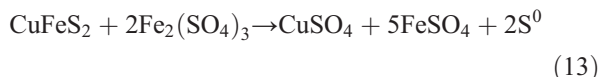
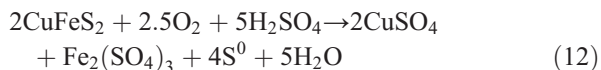
The combination of ultra-fine grinding (to 5–15  $\mu\text{m}$ ) and low temperature (100–110 °C) are the cornerstones of the ACTIVOX® process (Corrans and Angove, 1993, 1996, 1999; Johnson and Streltsova, 1999; Palmer and Johnson, 2005 and references therein; Streltsova and Johnson, 2003). The initial work on this process with chalcopryrite concentrate and *ca* 1000 kPa oxygen partial pressure, reported >90% copper extraction with an oxygen consumption of 0.99 kg per kg of copper leached (Corrans and Angove, 1993). This compares with a theoretical oxygen requirement of 2.4 kg per kg of copper leached if all of the sulfide sulfur is converted to sulfate.

Subsequently the addition of between 2 and 10 g/L chloride ion was recommended and patented (Johnson and Streltsova, 1999) in combination with ultra-fine milling to a  $P_{80}$  of between 2 and 20  $\mu\text{m}$  enabling up to 98% copper extraction within 45–60 min. The use of chloride ion to promote the low temperature leaching of chalcopryrite dates back to work by INCO (Subramanian and Ferrajuolo, 1976) and was also a key element of the DEXTEC process (Everett, 1978).

With the proven success of the ACTIVOX® process (Palmer and Johnson, 2005), a demonstration plant was built and assembled at the Tati Nickel mine site in Botswana. This is underpinned by an energy requirement of around 40 kWh per tonne for the ultra-fine milling of copper concentrate from a  $F_{80}$  of 60  $\mu\text{m}$  to  $P_{80}$  of 6  $\mu\text{m}$  which is almost an order of magnitude less than that quoted for the Lurgi–Mitterberg process.

## 5.2. Chemistry

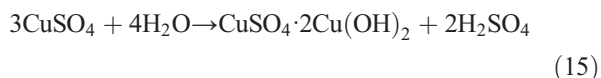
The chemistry of chalcopryrite oxidation at low temperatures is more complex since a large fraction of the sulfide is oxidised to elemental sulfur. Typical reactions that take into account the production of sulfur include:



Hydrolysis to form (hydronium) jarosite occurs via Eq. (6) and to form goethite:



Loss of copper from solution in the presence of sufficient sulfate can result in the formation of antlerite (Jones, 1996):



Most of the iron precipitates as goethite ( $\alpha\text{-FeOOH}$ ) or, in the presence of chloride ions, the related mineral akaganéite ( $\beta\text{-FeOOH}$ ) which incorporates a small amount of chloride into its structure, unless alkali ions are added, resulting in the preferred formation of jarosite. Depending upon the mineralogy of the concentrates and reaction conditions, the conversion of sulfide to elemental sulfur varies between 40 and 80% (Palmer and Johnson, 2005).



### 5.3. Low temperature results

#### 5.3.1. Effect of initial acid concentration and chloride ion addition

The extraction of copper from the chalcopyrite concentrate under Activox<sup>®</sup> conditions was successful in all instances where 10 g/L chloride ion was added to the system. The extraction data do, however, indicate that a significant amount of copper remains in some residues and this corresponded with the formation of basic copper salts (see Section 6.2).

When no acid was present initially, there was an induction period of approximately 30 min until a small amount of acid had been generated and significant leaching of the copper occurred (Fig. 7). Even in the absence of added chloride ion, the presence of even a small amount of acid was sufficient to commence leaching. However, in this instance a significant proportion of the chalcopyrite remained un-leached at the conclusion of the reaction. The presence of chloride ion was clearly critical for good extraction kinetics although its exact role and mechanism is unclear; sulfuric acid also appears to play an important part in the leaching of copper from chalcopyrite.

With no or low acid addition the final residue produced in the presence of chloride ion contained no detectable chalcopyrite. It was also found that during the early stages of the reaction, the basic copper chloride atacamite,  $\text{Cu}_2(\text{OH})_3\text{Cl}$ , was formed and that as the sulfate concentration increased (see Fig. 8) the bulk of the leached copper remained in the residue but was converted to the basic copper sulfate, antlerite,  $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ . These observations are consistent with the data published by Mann and Deutscher (1977)

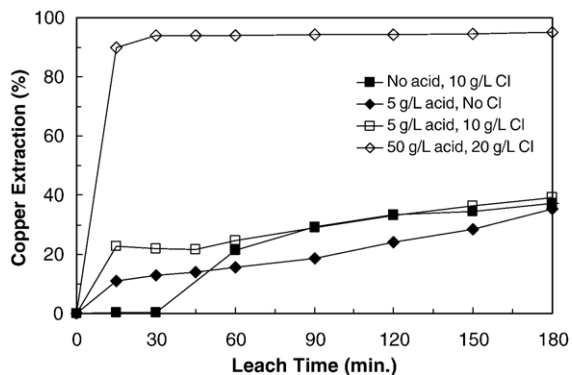


Fig. 7. Copper extraction from a 10% w/w chalcopyrite concentrate slurry using  $\text{P}(\text{O}_2)$  of 700 kPa at 108 °C with various sulfuric acid and sodium chloride additions (Activox<sup>®</sup> conditions).

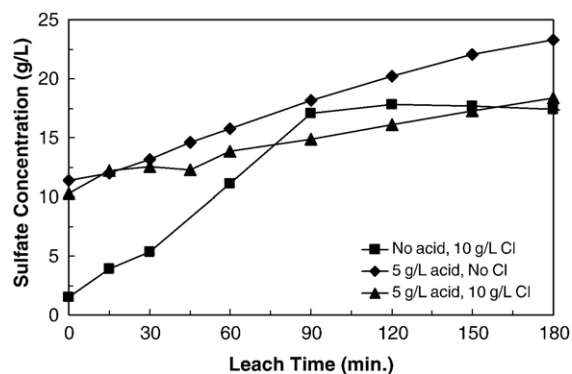


Fig. 8. Sulfate concentrations during the leaching of 10% w/w chalcopyrite concentrate slurry using  $\text{P}(\text{O}_2)$  of 700 kPa at 108 °C with various sulfuric acid and sodium chloride additions (Activox<sup>®</sup> conditions). Note that the sulfate concentration has increased during autoclave heating.

on the stability of atacamite and antlerite in mixed sulfate/chloride systems.

Re-leaching of the residues with a weakly acidic solution of pH 1.5–2.0 was sufficient to dissolve the antlerite to give a copper-containing solution and a washed residue containing 0.8% copper. This corresponded to an overall copper extraction of 96%.

The nature of the basic copper salts is expected to be critical if re-leach solutions are to be subsequently processed by electrowinning. If the chloride content of the salts is minimized, by the addition of sulfuric acid, the potential for the production of chlorine gas in the cell room is reduced. Furthermore this allows chloride to be recycled to the leach circuit and reduces any top-up requirement. Acid addition should, however, be kept to a minimum to optimise the amount of copper precipitated.

Not surprisingly, the antlerite and atacamite phases did not form when the initial acid concentration was increased to 50 g/L, resulting in a final copper extraction of over 94% after just 30 min of leaching. Since the final leach residue in this instance contained a trace of un-reacted chalcopyrite, it appears that sulfur formation affected the extraction of the last fraction of copper.

Measurements indicated that a liquor pH of 1.5 was sufficient to keep all of the copper in solution. Even when a high initial acid addition, 50 g/L, was employed, the free acid concentration dropped significantly, to about 5 g/L, during the first 15 min of the reaction. This was consistent with the preferential formation of sodium jarosite over hydrated iron oxides (e.g. akaganéite) as confirmed by the QXRD data (see Section 6.2).

The extraction of iron was generally low (Fig. 9) in keeping with the low free acidity of the leach liquor. In particular when the leach liquor pH increased to over 3.5, the iron levels fell to below 0.2 mg/L. It is arguable,

however, that by performing an Activox<sup>®</sup> leach under more acidic starting conditions residues such as sodium jarosite, which is expected to have better settling properties than phases such as goethite, akaganéite and their precursors (e.g. ferrihydrite), will be produced. On the flip side, most (if not all) of the copper will reside in solution whereas the iron levels will be higher, *ca* 1.0–1.5 g/L.

### 5.3.2. Sulfur oxidation

The calculated conversions of sulfide to elemental sulfur and sulfate under Activox<sup>®</sup> conditions are presented in Table 2. The high conversions of sulfide to sulfur rather than sulfate (and hence sulfuric acid) were consistent with the low liquor free acidities, which were typically less than 5 g/L. The low total oxidation of sulfur when chloride ion was absent was consistent with the low copper extraction and high un-reacted sulfide composition of the residue. However, the oxidation of sulfide to sulfate, rather than sulfur, occurred at a relatively more rapid rate. Clearly, the presence of chloride plays a role in suppressing the rate of sulfate production, for example by slowing the rate of elemental sulfur oxidation, as noted previously.

## 6. XRD analysis of leach residues

A large number of XRD patterns were obtained in the present study to characterise the leach residues formed. As it is not feasible to reproduce all the results here, selected examples of QXRD analyses are presented.

### 6.1. Leach residues from Phelps Dodge-Placer Dome conditions

High temperature processing effectively leached chalcopyrite, pyrite and the small amount of the clay

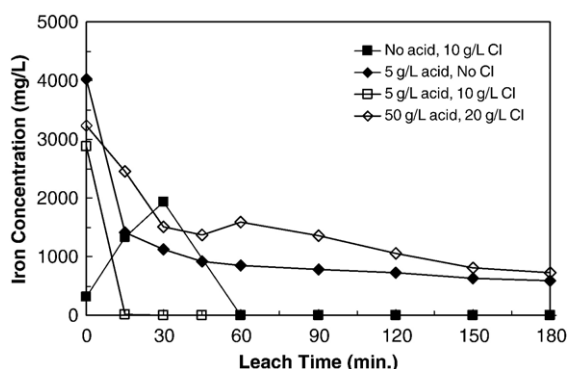


Fig. 9. Total iron concentrations during the leaching of 10% w/w chalcopyrite concentrate slurry using P(O<sub>2</sub>) of 700 kPa at 108 °C with various sulfuric acid and sodium chloride additions (Activox<sup>®</sup> conditions).

Table 2

Estimated conversions of sulfide to elemental sulfur and sulfate under Activox<sup>®</sup> conditions

Activox <sup>®</sup> experiment	(% conversion)	
	Sulfur	Sulfate
No acid, 10 g/L chloride	81	14
5 g/L acid, no chloride	20	11
5 g/L acid, 10 g/L chloride	79	14
50 g/L acid, 20 g/L chloride	89	8

mineral clinocllore that were present in the chalcopyrite concentrate. Quartz and talc were essentially unleached. The dominant mineral phase formed was hematite, and the conversion of sulfide to sulfate and dissolution of copper meant that the quartz composition in the residues increased. The changing mineral compositions during the Phelps Dodge-Placer Dome-type reactions at 220 °C when a pulp density of 20% was employed are shown in Fig. 10(a) and (b), with the addition of sodium chloride. The mineralogy of selected leach residues as determined by QXRD analysis is presented in Table 3.

While hematite was exclusively the final iron-containing product formed at low pulp density (10%) over the temperature range 180–220 °C, jarosite was also formed at higher pulp density and in the presence of sodium ions (Fig. 10(a) and (b)). In addition, trace elemental sulfur was noted in the intermediate residues formed at 180–190 °C. The formation of hematite (that produced some scaling) from the total oxidation of chalcopyrite concentrate at temperatures of 215–230 °C and pulp density of 10% was also noted by Marsden et al. (2003). It is interesting to note that the final ratios of hematite to jarosite formed at 220 °C are significantly higher than that found in the residues produced from the HPAL of nickel laterites at 250 °C even when sodium ions are present (Whittington et al., 2003). This is also not withstanding the fact that the formation of hematite becomes more preferable to (hydronium) jarosite with increasing temperature (Tozawa and Sasaki, 1986). Clearly the difference between the current pressure leaching and HPAL experiments is determined by the higher content of soluble aluminium in nickel laterites, most of which is ultimately re-precipitated as more stable aluminium-rich jarosite phases.

When the pulp density was increased to 20%, chalcopyrite (and pyrite) persisted in the leach residues for longer (Fig. 10(a)). A reasonable amount of (hydronium) jarosite and a small amount of basic ferric sulfate were produced after 30 min when the free acidity rose above 80 g/L (Fig. 5), although hematite was still the major iron-containing phase. With the addition of

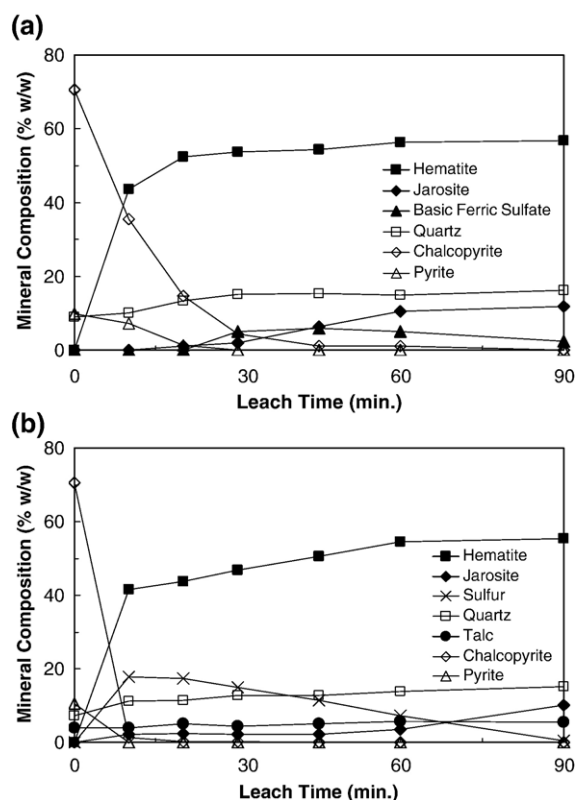


Fig. 10. (a) Leach residue mineralogy from a 20% w/w chalcopyrite concentrate slurry processed using  $P(O_2)$  of 700 kPa at 220 °C. The minor un-reacted talc component has been removed for clarity. (b) Leach residue mineralogy as for (a) but processed with the addition of 25 g/L NaCl.

25 g/L sodium chloride to the process water, chalcopyrite and pyrite were initially leached at a much more rapid rate (Fig. 10(b)). Again hematite was the major

iron-containing phase, and although a higher jarosite content was expected given that sodium jarosite is more stable than hydronium jarosite (e.g. Dutrizac and Jambor, 2000), this was not the case (Table 3). Rather, the composition of sodium jarosite only started to increase noticeably during the last 30 min of the reaction — which is consistent with a low driving force earlier in the reaction (i.e. low acidity).

The main effect of sodium chloride addition was to slow the oxidation of sulfur to sulfuric acid (and perhaps to promote the formation of sulfur over other oxidised sulfur species). This meant that the free acidity did not exceed a value of 80 g/L until after 60 min reaction time. Until this time sulfur was present in the leach residue in significant amounts (Figs. 6 and 10(b)) even though the chalcopyrite was completely leached. As noted previously, this confirms that the leaching of copper and the formation of sulfate do not necessarily occur in parallel.

## 6.2. Leach residues from Activox® conditions

Most Activox® residues were produced under conditions of low initial and on-going acidity with the pH of the liquors generally being above 3.0 and often close to 4.0. Furthermore, the concentration of sulfate was low initially and slowly increased as leaching occurred. As discussed previously, such conditions were conducive to the formation of basic copper salts and several were identified from XRD including atacamite, antlerite and in one instance, a trace of brochantite ( $Cu_4(SO_4)(OH)_6$ ). The veracity of the QXRD data for these phases was confirmed by comparing the calculated elemental composition of leach residues with the analytical data. In particular, the agreement for copper was generally

Table 3

QXRD analyses of leach residues (after 30 min and at the reaction conclusion) for leaching experiments performed under Phelps Dodge-Placer Dome conditions

Sample time (min.)	Temp. (°C)	Pulp density (% w/w)	Additives	Chalcopyrite	Pyrite	Hematite	Jarosite	Sulfur	Quartz	Talc
30	220	10	5 g/L $H_2SO_4$	ND	ND	58.0	ND	ND	15.7	5.0
90				ND	ND	60.7	ND	ND	15.7	5.6
30	200	10	5 g/L $H_2SO_4$	9.1	2.2	51.3	ND	ND	16.7	4.9
90				ND	ND	60.7	ND	ND	17.3	5.4
30	190	10	Nil	43.7	1.9	28.7	ND	ND	10.2	4.2
90				14.1	ND	51.6	ND	ND	14.2	5.7
30	180	10	Nil	60.3	5.4	10.0	ND	1.3	6.4	2.4
150				29.2	ND	49.8	ND	ND	17.5	5.4
30	220	10	5 g/L $H_2SO_4$	ND	ND	53.7	ND	ND	22.3	2.0
90				ND	ND	56.8	ND	ND	21.9	4.8
30*	220	20	5 g/L $H_2SO_4$	4.5	ND	45.3	1.9	ND	15.2	5.8
90^				ND	ND	50.6	11.8	ND	16.3	6.1
30	220	20	10 g/L Na as NaCl	ND	ND	46.9	2.1	14.9	12.8	4.3
90				ND	ND	55.3	10.2	0.4	15.3	5.5

ND: Not detected; \* and ^ residues also contain basic ferric sulfate, 5.1% and 3.1%, respectively.

excellent whereas the correlation for iron varied depending upon the iron-containing phases present.

In the presence of 10 g/L chloride ion, it was previously noted that there is an induction period, during which iron is released, before copper begins to appear in solution at significant levels. The XRD data suggest that during this period a large proportion of the chalcopryite is converted to a covellite-like phase. The peaks could be well-produced by Rietveld analysis using a covellite ( $\text{CuS}$ ) crystal structure ( $a=3.785 \text{ \AA}$ ,  $c=16.348 \text{ \AA}$ ) and a broad peak width. Once copper leaching commenced the “covellite” and remaining chalcopryite were rapidly consumed (Fig. 11(a)).

The addition of a small amount of acid at the beginning of the reaction favoured the formation of jarosite over goethite (Fig. 11(b)). However, a significant proportion of the iron-containing residue was either non-crystalline or poorly crystalline, and is included in the material referred to as “unaccounted”. The presence of intense, broad humps centred at diffraction angles of  $40\text{--}42^\circ$  and  $75^\circ 2\theta$  suggested the presence of at least 2-line ferrihydrite. The presence of other poorly crystalline iron(III) oxyhydroxide phases of higher symmetry (e.g. schwertmannite, 6-line ferrihydrite), however, cannot be discounted.

With the initial addition of 50 g/L sulfuric acid and 20 g/L chloride ion as sodium chloride a significant proportion of the iron-containing residue, particularly in the early samples, was again either non-crystalline or poorly crystalline (Fig. 11(c)). In addition no antlerite or atacamite were present, consistent with the lower pH of the system. Inspection of the XRD trace revealed not only an intense, broad hump centred at a diffraction angle of  $40\text{--}42^\circ 2\theta$  but also a smaller hump centred at  $14^\circ 2\theta$ . The difference between the Rietveld calculated pattern and the experimental data also suggested a significant hump at  $31^\circ 2\theta$  which in combination with the other two are characteristic of akaganéite ( $\beta\text{-FeOOH}$ ). This iron(III) oxyhydroxide forms in the presence of chloride ion and can contain up to 8% chloride (Chambaere and De Grave, 1984). The formation of this material in the higher chloride medium is not unreasonable, although iron, chloride and acid concentrations can all affect the type of iron(III) oxyhydroxide that is formed (Matijević and Scheiner, 1978).

The inclusion of akaganéite into the Rietveld analysis not only improved the calculated fit but also the agreement between the calculated iron content and analysis. Employing the structure  $\text{FeO}_2\text{Cl}_{0.21}\text{H}_{0.66}$  of Post et al. (2003), the akaganéite composition in the  $t=45$  sample was calculated to be 20% and the refined crystal structure parameters,  $a=10.65 \text{ \AA}$ ,  $b=3.03 \text{ \AA}$ ,  $c=10.37 \text{ \AA}$

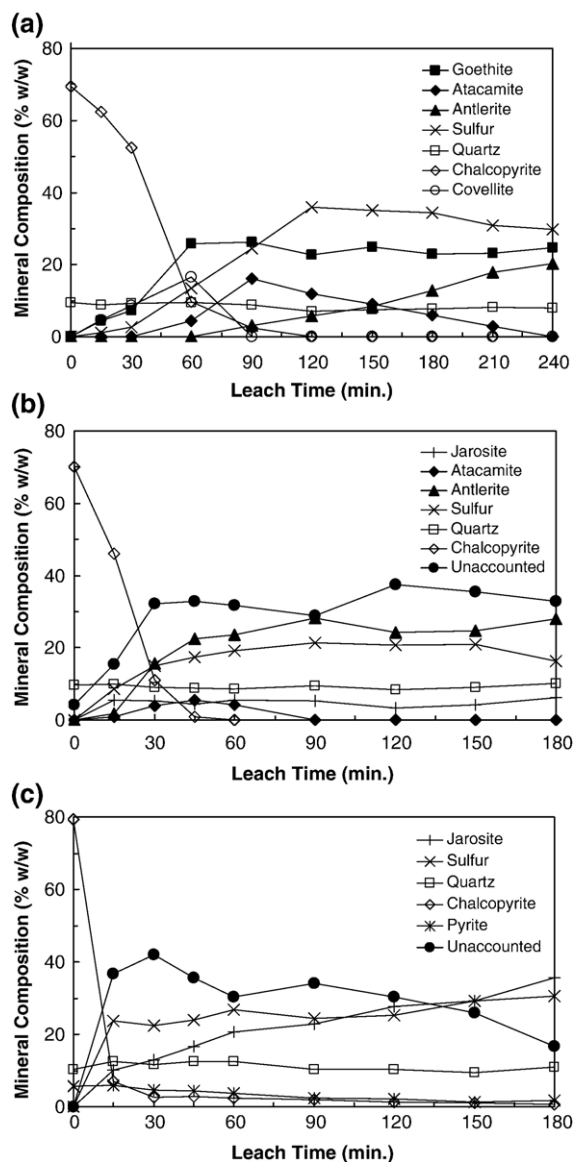
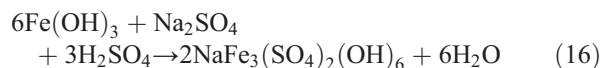


Fig. 11. (a) Leach residue mineralogy from a 10% w/w chalcopryite concentrate slurry processed with the addition of 10 g/L  $\text{Cl}^-$  as NaCl and using  $\text{P}(\text{O}_2)$  of 700 kPa at  $108^\circ\text{C}$ . The talc and pyrite components have been removed for clarity. (b) Leach residue mineralogy as for (a) but processed with the addition of 10 g/L  $\text{Cl}^-$  as NaCl, 5 g/L  $\text{H}_2\text{SO}_4$  and 3 g/L Cu as  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ . A significant proportion of the unaccounted material was ascribed to poorly crystalline hydrated iron oxides (see text). (c) Leach residue mineralogy as for (a) but processed with the addition of 20 g/L  $\text{Cl}^-$  as NaCl, 50 g/L  $\text{H}_2\text{SO}_4$  and 3 g/L Cu as  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ . A significant proportion of the unaccounted material was ascribed to akaganéite (see text).

and  $\beta=90.4^\circ$ , were in good agreement. Further studies are required to fully characterise akaganéite (and amorphous iron oxides) in pressure oxidation leaching residues and examine the conditions under which these are formed.



During the reaction the intensity of the hump at 40–42° 2 $\theta$  appeared to decrease, the composition of jarosite increased (Fig. 11(c)) and the agreement between the XRD calculated and actual iron content of the residue improved. Conditioning the residue appeared to convert some of the hydrated iron oxide to sodium jarosite according to the following equation:

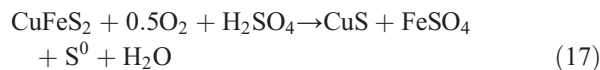


However, this reaction was not strongly favoured, despite the relatively high sodium and sulfate concentrations, because the free acidity level was quite low, typically 6–8 g/L. More acid must be added to the system or the extent of sulfur oxidation increased, to improve jarosite formation. This would then be expected to enhance the settling characteristics of the residue.

In contrast with higher temperature processes, both the pyrite and clinocllore components of the chalcopyrite concentrate reacted slowly under Activox® conditions. This reduced the oxygen requirement for leaching, suggesting that concentrates with higher pyrite content would be more economically treated by this process.

### 6.3. Formation of iron-deficient copper sulfide phases

In the presence of 10 g/L chloride ion, it was previously noted that there is an induction period, during which iron is released, before copper begins to appear in solution at significant levels (Section 5.3.1). On the basis that “covellite” is formed, the following reactions are proposed to explain its formation and disappearance:



The hydrothermal enrichment of chalcopyrite under various conditions has been reported by several other groups (Sohn and Wadsworth, 1985; Peterson and Wadsworth, 1994; Bartlett, 1992; Parker et al., 2003). Both Sohn and Wadsworth (1985) and Peterson and Wadsworth (1994) reported that the enrichment of chalcopyrite in the presence of cupric sulfate at temperatures of 125–200 °C under oxidising and non-oxidising conditions proceeds via the formation of covellite and subsequently digenite ( $\text{Cu}_{1.8}\text{S}$ ) with uptake of copper and the rejection of iron to solution. These studies compare with the hydrothermal enrichment of chalcopyrite to produce digenite ( $\text{Cu}_{1.8}\text{S}$ ) at temperatures

above 200 °C during which it is understood that the oxygen transfer rate to the mineral is not fast enough to maintain a high oxidation potential in the slurry (Bartlett, 1992). The leaching of digenite in oxygenated chloride media at 90–100 °C was reported to proceed in two stages. The first involved transformation to covellite and the second, dissolution of the covellite to give cupric ions and elemental sulfur (Ruiz et al., 1998).

Recently Parker et al. (2003) employed Raman spectroscopy to identify products formed during the oxidation of chalcopyrite. In addition to covellite, a small amount of idaite ( $\text{Cu}_5\text{FeS}_6$ ) was identified and a metal-deficient phase with S–S bonds that give rise to a Raman shift different from that for S–S stretch in covellite. Further work is required to better characterise the intermediate copper sulfide phases formed in the present study.

## 7. Conclusions

A selection of pressure oxidation leaching conditions has been evaluated with a chalcopyrite concentrate. Specifically, the Activox® and Phelps Dodge-Placer Dome process conditions have been investigated at temperatures of 108 °C and ranging between 180 °C to 220 °C, and in the presence of sodium chloride. At low temperature, copper extractions were optimised by fine grinding, and additions of sulfuric acid and chloride ion. Copper extractions of over 94% were achieved over time periods ranging between 10 and 30 min — though at lower temperatures, extraction of the residual copper took substantially longer. This was thought to be due to passivation of the chalcopyrite surfaces by metal-deficient polysulfide and/or sulfur. Overall, the chalcopyrite concentrate proved relatively easy to leach and the choice of process would depend upon a combination of factors such as the (1) cost of oxygen, (2) cost of ultra-fine grinding if required, (3) cost and availability of neutralising agents for acid or use of spent acid (e.g. heap leaching), (4) cost and availability of electricity, (5) availability of suitable process water, (6) method for copper recovery (SX-EW versus direct EW of copper re-leach solution) and (7) characteristics of the leach residue (e.g. settling, stability).

Changing the process conditions was found to have a significant impact upon (1) the conversion of sulfide to sulfur and/or sulfate and therefore the oxygen requirement, (2) the phases found in the leach residue and (3) the production of basic copper salts. The oxidation of sulfide to elemental sulfur was typically, 80–90% at low temperature whereas at temperatures of 180 °C and above, sulfate was exclusively produced. In the presence

of added sodium chloride, however, the oxidation of sulfur to sulfate was slower, enabling sulfur to be detected in leach residues produced at 220 °C. This could be detrimental when acid by-product is needed, residues are required to be treated to recover gold and silver, or when direct EW is necessary.

At high temperatures and when low pulp density pulps were processed, hematite was the dominant phase in the leach residue. Increasing the process acidity by increasing the pulp density favoured the production of other iron-containing phases such as (hydronium) jarosite and basic ferric sulfate. The addition of sodium ions stabilised natrojarosite production. While changes to the process water had a significant effect upon the composition of the leach residue it caused only minor variations in the final copper extraction. However, a significant change to the initial leaching rate was noted when sodium chloride was present.

Basic copper salts were produced under Activox® conditions in the presence of added chloride ions. When the sulfate level was low, atacamite was precipitated, whereas when sufficient sulfate was added or generated during leaching, antlerite was formed. Maintaining a low acidity also promoted the formation of goethite whereas an increase in acidity and the addition of sodium chloride favoured jarosite production, as well as keeping the copper in solution. Amorphous iron precipitates were also generated though these would be expected to have a negative impact upon solid–liquid separation.

## Acknowledgements

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