



Review

Chalcopyrite hydrometallurgy at atmospheric pressure: 2. Review of acidic chloride process options



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ABSTRACT

Hydrometallurgical process developments for the extraction of copper from chalcopyrite tend to target complex concentrates, dirty concentrates that would incur penalties if smelted or low-grade ores that are thus far an un-economic source of copper. Perceived advantages of chloride systems are the higher solubilities of copper and iron, the ease of ferrous ion oxidation and faster leaching kinetics of chalcopyrite compared with ferric sulfate systems, and the generation of sulfur rather than sulfate as the product of sulfide oxidation. Process developments for concentrates employ acidic, oxidising leach media containing sodium or other chloride salts and temperatures up to the boiling points of the high-concentration solutions. In those processes, chloride ion is thought to be an active agent in the dissolution mechanism. Leaching conditions fall into two groups, those targeting Cu(II) and those targeting Cu(I) in pregnant leach solutions. For low grade ores, usually processed in heaps, the use of seawater or other naturally saline water in leaching operations may be an 'economic' choice to overcome the scarcity and/or cost of freshwater. Few studies have been published describing the advantages and disadvantages of seawater substitution for freshwater in leaching processes but, from the sparse information available, seawater appears to be as efficient a solvent and carrier of acid and oxidant as freshwater. The recent descriptions of some iron(II)- and sulfur-oxidising, salt-tolerant acidophilic microorganisms indicate that a diverse group of microorganisms that could function in sulfide heaps irrigated with seawater await discovery. With regard to processing using seawater instead of freshwater, the salt content in seawater would impact directly on solution transport costs to and round a mine (through increased solution viscosity and specific gravity) and could adversely affect product and by-product purity.

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1. Introduction

The need to process low-grade and/or complex chalcopyrite-containing ores (see Table 1 for minerals referred to in the text and their ideal formulae) that cannot be concentrated has been the main driver for the development of hydrometallurgical processes. Other drivers are the current imbalance between copper supply and demand, the overall decline in ore grades and the extensive exploitation of low-grade oxide and secondary sulfide ores that may eventually leave large quantities of low-grade chalcopyrite ores as a major but, thus far, uneconomic source of copper. Typically, for large near-surface deposits, average copper cut-off grade for conventional processing is approximately 0.4% Cu (British Geological Survey, 2007), from which it may be deduced that the term “low grade” refers to ores with <0.4% Cu.

This review comprises the second part of an update on the status of copper extraction from chalcopyrite under atmospheric conditions, either in concentrated form or in low-grade ores. In the first part, sulfate-based systems operated at atmospheric pressure were described and compared (Watling, 2013 and references therein), with the aim of informing researchers, metallurgists and plant operators of the wide variety of chemical systems that might be applied in the future. This second part of the review is focused on the use of chloride systems for the extraction of copper from chalcopyrite. Developments using chloride fall into two groups, (i) those employing acidic, oxidising leach media containing sodium or other chloride salts up to concentrations encountered in brines, at temperatures up to the boiling points of the selected solution compositions (e.g., Hyvärinen and Hämäläinen, 2005) and (ii) those in which naturally saline water is substituted for freshwater water in leaching operations where freshwater is scarce

Table 1
Minerals and their ideal formulae.

Copper minerals	Ideal formula
Bornite	Cu ₅ FeS ₄
Chalcocite	Cu ₂ S
Chalcopyrite	CuFeS ₂
Covellite	CuS
Other minerals	
Albite	NaAlSi ₃ O ₈
Alunite ^a	KAl ₃ (SO ₄) ₂ (OH) ₆
Ferrihydrite	5Fe ₂ O ₃ ·9H ₂ O
Goethite	FeOOH
Gypsum	CaSO ₄ ·2H ₂ O
Hematite	Fe ₂ O ₃
Jarosite ^a	KFe ₃ (SO ₄) ₂ (OH) ₆
Magnetite	Fe ₃ O ₄
Marcasite	FeS ₂
Muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH, F) ₂
Phlogopite	KMg ₃ (Si ₃ Al)O ₁₀ (OH, F) ₂
Pyrite	FeS ₂
Pyrrhotite	Fe _{1-x} S (x = 0–2)
Schwertmannite	Fe ₈ O ₈ (OH) ₆ (SO ₄)·nH ₂ O
Silica ^b	SiO ₂
Vermiculite	(Mg, Fe, Al) ₃ (Al, Si) ₄ O ₁₀ (OH) ₂ ·4H ₂ O
Zeolite (natrolite)	Na ₂ Al ₂ Si ₃ O ₁₀ ·2H ₂ O

^a Potassium or other monovalent cations.

^b Silica varieties include amorphous, colloidal and gel.

(e.g., Dreisinger, 2009). Fundamental studies on the mechanisms of chloride leaching have been a common feature of process development among the first group of processes but are largely absent from the few processes involving the substitution of saline water for freshwater.

1.1. Sulfate systems revisited

The first part of the review covered the extraction of copper from chalcopyrite using sulfate, sulfate–chloride or sulfate–nitrate leach media (Watling, 2013). In summary, many studies generated data consistent with leaching rates being largely independent of acid concentration beyond that required to solubilise a sufficient concentration of ferric ions to react with available chalcopyrite surfaces, but dependent on sulfate concentration and solution oxidation reduction potential (ORP), the optimum ORP being dependent on ferrous ion and cupric ion concentrations. Topics concerning the influence of chalcopyrite crystallographic structure and the formation of secondary overlayers on chalcopyrite surfaces were also discussed. Copper extraction rates were enhanced by increased temperature, the presence of some microorganisms or by the addition of a chloride salt. However, sulfate processes with the addition of nitric acid or a nitrate salt were less well developed and the potential benefits remain poorly defined at this time. The efficiencies of sulfate leaching systems with superior-strength oxidants (compared with ferric ions) were discussed. For the most part, these were studied at laboratory scale but are yet to be exploited at commercial scale. The selected alternative oxidants were more costly than ferric ions, but some offered advantages in terms of extraction efficiency and kinetics, and further studies are warranted.

1.2. Scope of this review

In this second part of the review on chalcopyrite hydrometallurgy at atmospheric pressure, chloride-based leaching systems are described and compared. The majority of those processes targeted the processing of copper concentrates and were operated at atmospheric pressure and at temperatures approaching the boiling point of ferric chloride solutions (Table 2). A few higher-temperature processes conducted in pressure vessels have also been described by McDonald and Muir (2007a, b) and the effects of adding sodium chloride to them investigated. These pressure oxidation processes are not considered further in this review. No account is taken of the possible economics of processing, but rather the aim is to inform researchers, metallurgists and plant operators about the wide variety of chemical systems that might be applied in the future when copper demand is higher, ore grades are lower and new technologies, particularly for reagent recovery and recycle, have been developed. While the advantages or disadvantages of current technologies may be referred to in the context of reported results or applications of specific systems, detailed accounts of the engineering of such technologies, their management and/or control are outside the scope of the review.

2. Benefits and disadvantages of chloride leaching

The strong interest in chloride systems resides in: (i) the increased solubilities of iron and other metals; (ii) enhanced redox properties

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