

Copper extraction from chalcopyrite: Comparison of three non-sulfate oxidants, hypochlorous acid, sodium chlorate and potassium nitrate, with ferric sulfate



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ABSTRACT

Three oxidants, hypochlorous acid, chlorate and nitrate, were assessed for their ability to oxidise chalcopyrite (CuFeS_2). Hypochlorous acid was the most aggressive oxidant trialled, with copper extraction reaching a plateau after 1–5 h. Extraction in this system was complete at room temperature when reagent concentrations of 0.3–0.4 M were supplied. Optimal conditions utilising chlorate as an oxidant measured final extractions of 66–72% after 168 h. Optimal conditions utilising nitrate enabled a final extraction of 92% in systems using milled ore. Gangue dissolution in the presence of each oxidant varied. The system utilising nitrate resulted in comparatively high levels of magnesium and aluminium extraction, 28% and 32%, respectively. The chlorate system, over an identical time period and similar solution pH, had magnesium and aluminium extractions of 7% and 6%. These data, together with those for silicon dissolution, are indicative of incongruent silicate dissolution. Iron extraction data indicated that ferric hydroxy-oxide precipitates formed during leaching in both nitrate and chlorate systems. All systems tested offered improved rates of copper extraction relative to systems utilising ferric sulfate as an oxidant.

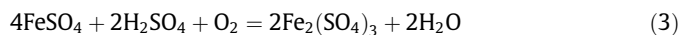
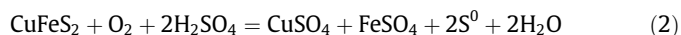
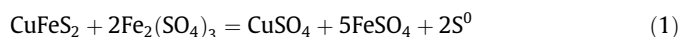
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1. Introduction

The overall limitations of the poor dissolution kinetics of chalcopyrite in ferric sulfate systems (with or without microorganisms – catalysts) drives the search for innovative ways to increase dissolution kinetics using different oxidants, different temperatures, controlled redox leaching, and pre-treatment of concentrates or ores. The purpose of this study is to describe copper extraction at atmospheric pressure in sulfate-free or minimal-sulfate media with selected oxidants other than ferric sulfate. The use of chalcopyrite concentrate for most tests permits comparisons of leaching rates in systems largely free of gangue minerals that might react with test reagents and obscure the targeted results.

The most commonly employed hydrometallurgical process for the oxidation of chalcopyrite and extraction of copper is the sulfuric acid–ferric sulfate system. Reactions (1)–(3) are the generally accepted reactions for the extraction of copper from chalcopyrite via oxidation (oxygen, ferric ions) or acid (H_2SO_4) leaching. It is the system of choice for bioleaching processes at atmospheric pressure, including stirred tank technologies for concentrates (Batty

and Rorke, 2006) and heap or dump technologies for low-grade ores (Watling, 2006). However, whether chemical or bio-assisted chemical leaching is undertaken, the oxidation of chalcopyrite is slow and incomplete, even if grains are exposed to solution.



The slow dissolution kinetics are thought to be consequences of the mineral crystalline structure and changes therein (Klauber, 2003; de Oliveira et al., 2012), or the formation of insoluble secondary reaction products (elemental sulfur, ferric hydroxysulfates or polysulfides) on chalcopyrite surfaces (Klauber, 2008). In summary, from a survey of the literature (Watling, 2013), dissolution rates are:

- proportional to CuFeS_2 surface area, strongly influenced by grain size and possibly influenced by crystal orientation of the surface exposed to the oxidant/lixiviant,
- independent of acid concentration as long as there is sufficient to keep ferric ions in solution,

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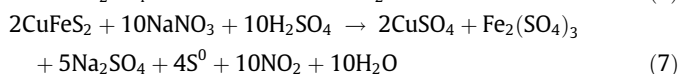
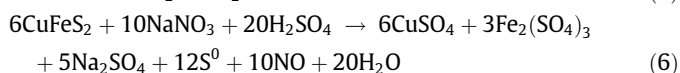
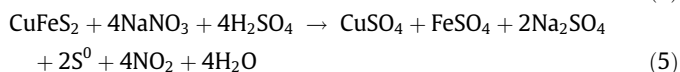
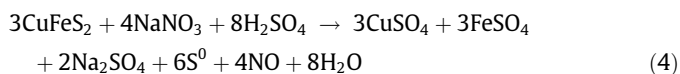
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- slightly dependent on Fe^{3+} concentrations but inhibited by increased sulfate ion concentrations,
- faster at mid-range oxidation–reduction potential (ORP) than at high ORP,
- enhanced in the presence of iron(II) oxidising *Bacteria* and *Archaea*, and
- strongly dependent on temperature in the range 25–100 °C at atmospheric pressure.

There have been numerous studies aimed at overcoming the slow dissolution kinetics, the vast majority employing chalcopyrite concentrate regardless of the intended material to be treated in the final process. The present study was focused on the use of alternative oxidants for the dissolution of chalcopyrite in mildly acidic conditions at atmospheric pressure. Background information for the study was obtained during the preparation of two substantive reviews of chalcopyrite oxidative dissolution (Watling, 2013, 2014). Noting that the passivation of chalcopyrite has commonly been attributed to three ‘sulfur-containing’ compounds (elemental sulfur, ferric hydroxysulfates or polysulfides), non-sulfate oxidising systems were chosen for the study. Rationalising that an alternative oxidant would need to be readily available commercially, the three oxidants selected for study were:

- nitrate-based; sodium nitrate (NaNO_3) is a mineral product of Chile;
- chlorate-based; NaClO_3 is used extensively in the paper industry for making chlorine dioxide; and
- hypochlorous acid-based (HClO), readily prepared by acidifying household bleach with HCl.

The selected alternative oxidants all have higher reduction potentials than ferric ion (Table 1). The literature pertaining to the use of each of these oxidants tested was reviewed recently (Watling, 2013, 2014). In brief, the benefits of using sodium nitrate were recognised more than 130 years ago (Stetefeldt, 1883) and a variety of processes have been proposed since then for application to *in situ*, dump and heap leaching as well as pressure leaching of copper sulfides, mainly using sulfuric acid (e.g., Sokić et al., 2009, 2010; Vračar et al., 2003). These authors provided comprehensive accounts of the chemistry of the systems tested. For CuFeS_2 , the reactions (4)–(7) with various stoichiometries were thought to occur (Sokić et al., 2010, 2014).



The strong oxidising power of NaClO_3 has been exploited mainly in the uranium industry (Edwards and Oliver, 2000) but was proposed as one of several possible oxidants for use in the production of other metals. Both the NaClO_3 – H_2SO_4 and NaClO_3 –HCl systems have been applied to the dissolution of CuFeS_2 (Kariuki et al., 2009; Xian et al., 2012). In the context of the present study on CuFeS_2 dissolution, Kariuki et al. (2009) studied CuFeS_2 leaching in sealed vessels in a sulfuric acid solution. They mixed chalcopyrite concentrate with up to NaClO_3 and then added H_2SO_4 (solution composition 0.9 M NaClO_3 , 0.1 M H_2SO_4 ; pH ~0.7). The results showed that CuFeS_2 oxidation (reaction (8)) increased with

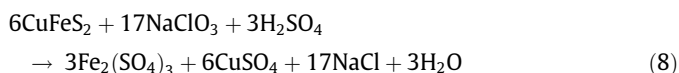
Table 1

Selected oxidants tested on chalcopyrite, half reactions and standard reduction potentials (Lide, 2008).

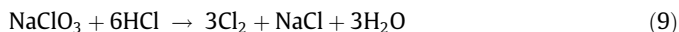
Oxidant	Half reaction	Standard reduction potential (E^0) (V)
Ferric ion	$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	0.771
Nitrate	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	0.957
Chlorate	$\text{ClO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow 3\text{H}_2\text{O} + 0.5\text{Cl}_2$	1.470
	$\text{ClO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} + \text{Cl}^-$	1.451
Hypochlorous acid	$\text{HClO} + \text{H}^+ + \text{e}^- \rightarrow 0.5\text{Cl}_2 + \text{H}_2\text{O}$	1.611
	$\text{HClO} + \text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O}$	1.482

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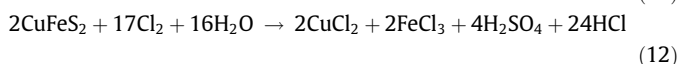
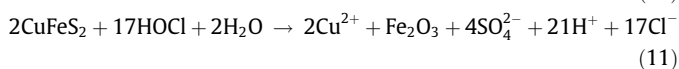
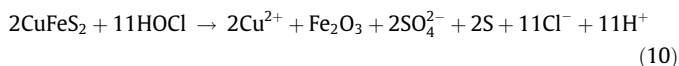
increased temperature in the range 45–100 °C. Assuming a stoichiometric reaction, the end result would be a solution containing 0.9 M Cl^- , sufficient to contribute to enhanced Cu extraction through the stabilisation of iron and copper complex ions but at a higher pH than the conditions of Carneiro and Leão (2007).



The presence of NaClO_3 was also reported to enhance the dissolution of CuFeS_2 in HCl solutions (Xian et al., 2012). At 45 °C, copper extractions after 5 h in solutions of 0.5 M and 1 M NaClO_3 in 1 M HCl were 45% and 65%, respectively (Xian et al., 2012). The leaching rate accelerated with increased HCl concentration up to 1.5 M. In addition to chlorate ion, the reaction products ferric chloride and gaseous Cl_2 (detected by odour during leaching; reaction (9)) could also have oxidised CuFeS_2 , but the stoichiometry of the reaction products indicated that the gaseous Cl_2 was more likely to have been volatilised. Surface area (grain size) was an important parameter in the study by Xian et al. (2012).



The application of aqueous hypochlorous acid to the oxidative dissolution of CuFeS_2 and other sulfide minerals is part of a reaction continuum from acid to alkaline conditions. Potential processes at low temperature and atmospheric pressure utilising hypochlorite anion in alkaline solutions (e.g., Garlapalli et al., 2010), hypochlorous acid in mildly acidic solutions (e.g., Ikiz et al., 2006) and aqueous chlorine in acidic solutions (e.g., Park et al., 2009) have been described. CuFeS_2 and other copper sulfides are amenable to one or more of these treatments. The advantages of using mildly acidic solutions are the extremely strong oxidative capacity, the selectivity towards sulfide minerals over gangue minerals and the minor extent of gangue mineral acid consumption. The hypochlorous acid leach, conducted at pH 4–6, beyond the stability zone of Fe^{3+} , follows reactions (10) and/or (11). At the slightly more acidic pH where hypochlorous acid decomposes to Cl_2 , the leach loses selectivity, causing iron to be solubilised as well as the copper (reaction (12)). Gaseous reagent loss is a disadvantage of the hypochlorous acid system, requiring the use of closed reactors.



Given that ferric ions in acidic solutions are the most commonly applied system for sulfide dissolution, comparative data pertaining to ferric ion as oxidant were also obtained using the experimental apparatus and conditions.

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