

# Response of thermophiles to the simultaneous addition of sulfur and ferric ion to enhance the bioleaching of chalcopyrite<sup>☆</sup>

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## Abstract

Previous studies identifying  $\text{Fe}^{3+}$  as the main oxidizing agent in  $\text{CuFeS}_2$  bioleaching suggests that if the precipitation of additional  $\text{Fe}^{3+}$  could be prevented, the Cu extraction yields should be enhanced. In this respect, the acid-generating nature of the biologically mediated oxidation of additional  $\text{S}^0$  to  $\text{H}_2\text{SO}_4$  should theoretically serve as a pH regulator as well as biomass generator. This should prevent the precipitation of  $\text{Fe}^{3+}$  and attenuate the biomass reduction caused by the inhibitory effect of high  $\text{Fe}^{3+}$  concentrations. To prove the former hypothesis, three thermophile strains were employed for bioleaching of chalcopyrite under various additional  $\text{S}^0$  and  $\text{Fe}^{3+}$  concentrations. The hypotheses about additional  $\text{S}^0$  application were fully confirmed; the addition of  $\text{S}^0$  alone enhanced the leaching rates with *A. brierleyi* and *M. sedula* in media at initial pH 2. Although higher initial leaching rates were obtained with additional  $\text{Fe}^{3+}$ , its role as the main leaching factor is questioned; leaching with thermophiles appears to depend on the availability of protons and ORP rather than on the prevention of  $\text{Fe}^{3+}$  precipitation. Additional  $\text{S}^0$  in media with high  $\text{Fe}^{3+}$  concentrations has shown the best improvements in the case of bioleaching with *A. brierleyi*, whereas improvements in bioleaching with *M. sedula* and *S. metallicus* were less notable.

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## 1. Introduction

The abundance of the copper-bearing chalcopyrite ( $\text{CuFeS}_2$ ) mineral has motivated considerable attempts toward the development of low-cost technologies such as bioleaching with mesophiles. However, limitations due to low copper extractions and low kinetics have limited its implementation on a commercial scale. In this respect, bioleaching with thermophiles has arisen as the most promising alternative to overcome the drawbacks inherent to bioleaching with mesophiles. However, despite the encouraging results obtained, particularly in laboratory-scale experiments, the performance of large-scale thermophilic bioleaching processes such as the BioCOP process (Batty

and Rorke, 2006) might still be prone to failure due to the precipitation of  $\text{Fe}^{3+}$  salts and probable inhibition of the thermophiles by  $\text{Fe}^{3+}$ .

Although the mineral characteristics cannot easily be adapted to prevent any failure caused by the composition of the medium, the composition of the leaching medium can certainly be controlled to give thermophiles appropriate conditions to attach to the  $\text{CuFeS}_2$  mineral. In this respect several attempts such as oxygen limitation (Third et al., 2002) and  $\text{Fe}^{2+}$  addition (Hiroyoshi et al., 2001) have been made to keep the oxidation reduction potential (ORP) of the leaching medium below a critical value (450 mV) where the leaching rate of  $\text{CuFeS}_2$  has been shown to be enhanced (Kametani and Aoki, 1985). However, the influence of the ORP on the leaching rate appears to be more closely related to chemical leaching than to bioleaching. Different responses to low ORP conditions have been reported for chemically and bioleached chalcopyrite (Sandstrom et al., 2005).

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Up to now, the presence of  $\text{Fe}^{3+}$  in the leaching medium has been widely accepted as the principal factor for the indirect leaching mechanism of  $\text{CuFeS}_2$  (Watling, 2006). However, the importance of other factors such as the properties of the extra-cellular polymeric substance (EPS) formed on the mineral surface is also recognized as important in bioleaching of sulfide minerals. Although the EPS formation has been studied mostly in the context of  $\text{FeS}_2$  bioleaching of mesophile bacteria rather than on bioleaching of thermophile archaea on  $\text{CuFeS}_2$ , the formation of EPS in  $\text{CuFeS}_2$  bioleaching has not been discarded (Rodríguez et al., 2003; Konishi et al., 1999). This zone might be where intermediate products such as  $\text{S}_2^{2-}$  and  $\text{S}_n^{2-}$  are formed and the apparent indirect leaching reaction mediated by  $\text{Fe}^{3+}$  take place (Sand et al., 2001). Therefore, any modification of the leaching medium needs to take into consideration the response of the existing thermophiles which, besides being in charge of the generation of  $\text{Fe}^{3+}$ , are also responsible for the formation of the leaching zone (EPS).

Besides intermediates such as disulfide ( $\text{S}_2^{2-}$ ) and polysulfide ( $\text{S}_n^{2-}$ ) species, X-ray photoelectron spectroscopy (XPS) characterization studies (Parker et al., 2003; Sandstrom et al., 2005) have confirmed elemental sulfur ( $\text{S}^0$ ) as the main intermediate product formed during chalcopyrite bioleaching. Its importance rests on the fact that sulfur and sulfate product barriers formed on the mineral surface cause a passivating effect on the leaching reactions. This phenomenon has been widely discussed in mesophilic bioleaching studies where  $\text{S}^0$  accumulation has been detected by XPS too. On the other hand, the passivating effect due to  $\text{S}^0$  accumulation appears to be negligible for the case of thermophilic bioleaching where the preference of thermophiles to oxidize  $\text{S}^0$  over  $\text{Fe}^{2+}$  effectively eliminates  $\text{S}^0$  accumulation on the mineral surface. The capacity of thermophiles to oxidize  $\text{S}^0$  which could otherwise have formed a passivating layer, has been proposed as an explanation for the improvements observed in  $\text{CuFeS}_2$  bioleaching using thermophiles (Jordan et al., 2006). However, it appears that even if the  $\text{S}^0$  formed is further oxidized to sulphuric acid, the protons formed are not sufficient for the demand of acid consumption reactions such as  $\text{CuFeS}_2$  leaching itself. Even in the case of bioleaching with thermophiles, passivation of the leaching process is still observed not due to  $\text{S}^0$  accumulation but due to iron-hydroxy compounds and particularly the precipitation of jarosite ( $\text{MFe}_3(\text{SO}_4)_2(\text{OH})_6$ ,  $\text{M}=\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ) caused by increases in the pH of the medium (Stott et al., 2000, 2001; Sandstrom et al., 2005).

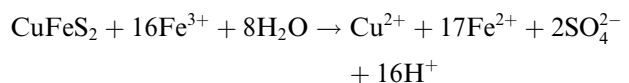
From previous studies, it is clear that chalcopyrite leaching is favoured at low ORP conditions (Third et al., 2002; Hiroyoshi et al., 2001; Sandstrom et al., 2005) but on the other hand it is also evident that constant low ORP conditions below a critical potential might be hardly maintained in media containing  $\text{Fe}^{2+}$  oxidizing entities such as mesophiles or thermophiles. Therefore, in this study we research into the feasibility of improving the copper extraction obtained with  $\text{Fe}^{3+}$  where  $\text{S}^0$  has been reported to form a

dense layer during the initial stage of the leaching reactions (Majima, 1995; Hirato et al., 1987). Although leaching of chalcopyrite with  $\text{Fe}^{3+}$  in sulfate media has been reported to be insensitive to  $\text{Fe}^{3+}$  concentrations higher than 0.01 M (Dutrillac, 1981), the question remains unsolved of whether the utilization of thermophiles capable of eliminating the  $\text{S}^0$  layer has any effect on the leaching kinetics in media containing  $\text{Fe}^{3+}$  concentrations higher than 0.01 M. From previous studies, it is also known that the  $\text{Fe}^{3+}$  formed by the reaction or added to the medium might lead to side-effects such as jarosite precipitation. In this respect, it is also still unclear whether the additional  $\text{S}^0$  oxidation to sulfate can generate enough protons to keep the pH of the medium below threshold values such that  $\text{Fe}^{3+}$  precipitation can be buffered throughout the leaching process, and whether the addition of  $\text{S}^0$  which is a more accessible source of energy than  $\text{CuFeS}_2$  can lead to higher biomass concentrations.

There are an appreciable number of thermophiles identified capable of carrying out bioleaching of  $\text{CuFeS}_2$ , because of their widespread occurrence and leaching capacity: *Acidianus brierleyi* (Seeger et al., 1986), *Sulfolobus metallicus* (Huber and Stetter, 1991) and *Metallosphaera sedula* (Huber et al., 1989) strains were selected for this study. Based on the response of these three representative thermophile strains, the aim of this work was to assess the feasibility of applying  $\text{S}^0$  such that the leaching passivation effects due to the additional and/or generated  $\text{Fe}^{3+}$  in the medium can be prevented, and insights into the fundamental mechanism of thermophilic bioleaching of  $\text{CuFeS}_2$  concentrates can be gained. The experimental approach consisted of an initial evaluation of the response of thermophiles to the separate additions of  $\text{S}^0$  and  $\text{Fe}^{3+}$ , followed by an evaluation of the response of thermophiles to the simultaneous addition of  $\text{S}^0$  and  $\text{Fe}^{3+}$ . Additional experiments under various pH conditions were also performed to determine the effect of proton availability on the bioleaching of  $\text{CuFeS}_2$ .

## 2. Background

In the light of an indirect mechanism, the sulfide content in the chalcopyrite mineral is oxidized to  $\text{S}^0$  directly by  $\text{Fe}^{3+}$  with the  $\text{S}^0$  formed being further biologically oxidized to sulfate: the whole reaction is sometimes represented as follows:



where  $\text{Fe}^{3+}$  is biologically regenerated from the released  $\text{Fe}^{2+}$ . In order to distinguish between the chemical and biological reactions involved in the indirect leaching mechanism, the leaching reaction of  $\text{CuFeS}_2$  is usually divided into an initial reaction where the sulfide in  $\text{CuFeS}_2$  is chemically oxidized to  $\text{S}^0$  by  $\text{Fe}^{3+}$  ( $r_1$ ), and into two biologically mediated reactions where the intermediates  $\text{S}^0$  and  $\text{Fe}^{2+}$

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