



# Thermodynamic modeling of atmospheric hydrometallurgical removal of chalcopyrite from molybdenite concentrates



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## ABSTRACT

Hydrometallurgical leaching is a critical step in reducing the impurity content of molybdenite concentrates; the removal of copper by this method has been widely studied from an industrial perspective. An understanding of the thermodynamic conditions leading to the removal of chalcopyrite from molybdenite concentrates is necessary to guide process optimization and future developments. Thermodynamic modeling software was used to identify process conditions for complete copper leaching in the traditional ferric chloride system, which agree with conditions typically used in industry; these were then extended to investigate alternative leaching reagents. Thermodynamic modeling, coupled with an understanding of process conditions, can guide future study.

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## 1. Introduction

Froth flotation is used to produce molybdenite ( $\text{MoS}_2$ ) concentrates typically containing ~48%–56% molybdenum (Mo); flotation is a critical step because it rejects much of the gangue material normally associated with  $\text{MoS}_2$  in the ore body. However, the simultaneous flotation of some minerals, like chalcopyrite ( $\text{CuFeS}_2$ ), whose surface properties are similar to those of  $\text{MoS}_2$ , cannot be sufficiently depressed to yield a high-quality final concentrate. Because  $\text{CuFeS}_2$  is often closely associated with  $\text{MoS}_2$  deposits, the concentrates produced by flotation often contain 1.0%–1.5% Cu; further removal of Cu in cleaner stages is largely considered uneconomical (Gupta, 1992). A high-quality  $\text{MoS}_2$  concentrate should contain no more than 0.15%–0.50% Cu. Therefore, concentrates are further processed to remove residual copper and other impurity metals. The most common technique to perform this separation is leaching.

Chalcopyrite is the most important Cu-bearing mineral encountered by the molybdenum industry and represents the major source of copper for copper producers. Other Cu-bearing minerals, typically oxides of the metal, are easily removed by leaching with sodium cyanide (Copper Leaching, 1979) or hydrochloric acid (HCl) (Dorbrick and Chen, 1972; Jennings et al., 1973; Zelikman et al., 1966). Chalcopyrite, however, presents a greater challenge and the processing route used in industry was originally developed at the Brenda Mines (Bradburn and Gratch, 1977; Haver et al., 1975). The Brenda Leach Process uses oxidizing chlorides, namely,  $\text{FeCl}_3$ —with  $\text{CuCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{NaCl}$  present—in an HCl medium

to remove  $\text{CuFeS}_2$ . The advantage to using  $\text{FeCl}_3$  in HCl is that the ferrous ions produced during leaching can be regenerated to ferric ions in a chlorinator operating in conjunction with the leaching process.

While the Brenda Leach Process has gained widespread acceptance, researchers have searched for alternative processing options. Sulfation (Yanatos and Antonucci, 2001) and sulfidation (Padilla et al., 2013) have been studied as a means to selectively remove copper from  $\text{MoS}_2$  concentrates with limited success. Alternative reagents have been investigated using different oxidants, like dichromate (Ruiz and Padilla, 1998). An area that has garnered particular interest is bioleaching, which echoes the process by which many copper piles are heap leached. Efforts have been made to identify the best conditions and best bacterial strains for copper removal (Abdollahi et al., 2014; Askari Zamani et al., 2006; Romano et al., 2001).

Work in developing novel leaching parameters has often involved bench-scale experiments testing a matrix of conditions. While important, especially in determining kinetic parameters, these efforts can be labor intensive and time consuming. Sophisticated thermodynamic modeling software, like the FactSage® package (Bale et al., 2013) used in this study, permit the rapid characterization of leaching equilibria under a multitude of conditions. While thermodynamic equilibria studies cannot entirely replace experimental work, they can significantly reduce time spent at the bench scale and offer insight into the thermodynamic condition of the system under evaluation. Thermodynamic modeling can guide developmental work by identifying critical process conditions, screening candidate reagents or operational parameters, and pinpointing equilibrium conditions. In this manner, the leaching of  $\text{MoS}_2$  concentrates to remove Cu in the form of  $\text{CuFeS}_2$  was investigated using FactSage® 6.4 in the hopes of identifying the prevalent conditions leading to successful Cu removal.

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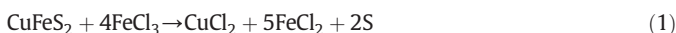
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## 2. Methods

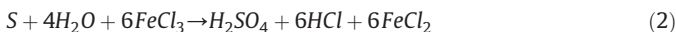
A hypothetical molybdenite concentrate containing 54% Mo and 1% Cu (90% MoS<sub>2</sub>, 7% SiO<sub>2</sub>, and 3% CuFeS<sub>2</sub>) was used in these studies; other impurities encountered during MoS<sub>2</sub> concentrate were not included. Typical impurities in a molybdenum concentrate are Pb, As, Bi, Fe, Sn, F, and alkali and alkali earth metals. During leaching operations, these impurities may consume acid and/or lixivants, form precipitates with leaching components, or present insoluble phases. The treatment of these species during leaching must be performed in subsequent studies but is outside the scope of the present work. A pulp density (mass to volume ratio) of 10% was used in all studies; studies were all performed at atmospheric pressure. FactSage® simulations were performed to determine the equilibrium leaching performance of different leaching agents.

## 3. Ferric chloride leaching of molybdenite concentrate

Gupta (1992) reports that the ideal leaching solution for CuFeS<sub>2</sub> removal from MoS<sub>2</sub> contains 30% CaCl<sub>2</sub>, 10% FeCl<sub>3</sub>, 3% HCl, and 1% CuCl<sub>2</sub> (all percentages are weight percentages). It is widely held that the leaching proceeds via Eq. (1).



In such a scheme, the calcium and copper salts present in the lixiviant are mere spectators. Often, the leach solution is recycled through a multipass system to reduce reagent consumption after the ferric ions are regenerated through chlorination (Gupta, 1992). It is apparent that the leaching reaction (Eq. (1)) is a redox scheme in which Cu(+1) and S(−2) are simultaneously oxidized while Fe(+3) is reduced; the HCl ensures the acidic conditions required for redox. A slow side reaction (Eq. (2)) is known to consume elemental sulfur. Temperatures are typically kept between 70°C and 80°C with finishing at elevated temperatures sometimes required.



The thermodynamic study of Eqs. (1) and (2), coupled with side reactions involving MoS<sub>2</sub>, will help guide understanding of better methods (1) to control and optimize leaching, (2) to reduce reagent consumption and/or improve operations, and (3) to identify alternative leaching reagents.

In this work, an initial leaching study with lixiviant at 1 M HCl (3.6%) and 0.5 M FeCl<sub>3</sub> (8.1%) at 75°C and 1 atm showed that the copper was completely leached. The ferric iron was also nearly completely reduced to ferrous. The potential and pH of the solution were 0.365 V and −0.078, respectively. While the leach was clearly successful under these conditions, it was also observed that 2.9% of the molybdenum charge was converted to MoO<sub>2</sub>. Depending on the application, this effect may negatively impact downstream production. For example, if the MoS<sub>2</sub> concentrate is to be used in producing lubricant grade sulfide material, the presence of MoO<sub>2</sub> can be detrimental. In general, molybdenum concentrates destined for lubricant production do not require leach treatments. It is well known that MoS<sub>2</sub> forms MoO<sub>2</sub> (and eventually MoO<sub>3</sub>) in acidic solutions (Gupta, 1992). Therefore, in an effort to reduce this effect and investigate whether reagent consumption can be decreased, further studies were performed.

At 75°C, it is interesting to note that while 100% of the CuFeS<sub>2</sub> was leached and no Cu solid remained, >98.9% of the copper existed as cuprous ions; the remaining 1.06% were fully oxidized to cupric ions (Fig. 1). Over the temperature range investigated, 2.85% of the Mo was converted to MoO<sub>2</sub>, and all Fe was present in solution in the ferrous form. As can be seen in Fig. 1, the amount of variation in Cu oxidation to cupric was very slight (<0.23%) with the maximum amount (<1.1%) occurring at 60°C. This observation stands in stark contrast to

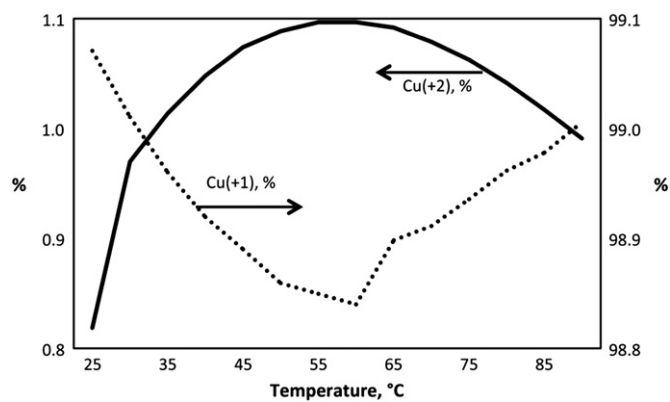


Fig. 1. Ratio of Cu(+1) to Cu(+2) in solution as a function of temperature, 1 M HCl and 0.5 M FeCl<sub>3</sub>; % Cu(+2) (solid), % Cu(+1) (dotted).

the stoichiometry presented in Eq. (1). Further, no elemental S was found in solution, with the majority (>99%) of the dissolved S present as the sulfate ion, in apparent agreement with Eq. (2). If the Cu component in CuFeS<sub>2</sub> is understood to be monovalent (Goh et al., 2006; Li et al., 2013; Pearce et al., 2006), these results suggest that CuFeS<sub>2</sub> is decomposed with Fe(+3) reduction and S(−2) oxidation while the Cu(+1) remains unoxidized. Alternatively, if the Cu in CuFeS<sub>2</sub> exists as Cu(+2), it must be reduced over the course of the leaching reaction, perhaps by sulfur. It is also possible that Cu exists in both mono- and divalent forms in CuFeS<sub>2</sub>, in which case both former mechanisms may be in action.

Under these initial conditions, moderate variations in the amount of HCl had no effect on MoS<sub>2</sub> conversion or leaching efficiency. However, at lower HCl concentrations (0.5 M, 1.8%), variations in the amount of FeCl<sub>3</sub> (0.1–0.5 M, 1.6–8.1%) were found to elicit changes in leaching efficiency and MoO<sub>2</sub> formation (Figs. 2 and 3).

At low FeCl<sub>3</sub> concentrations, the Cu content in the concentrate is too high. However, increasing the FeCl<sub>3</sub> concentration to approximately 0.22 M (3.6%) leaches 52% of the Cu from the concentrate and brings the impurity to 0.5%. A high-grade concentrate (0.15% Cu) can be achieved by increasing the FeCl<sub>3</sub> concentration to 0.26 M (4.2%). The residual Cu remaining in the concentrate is found to exist as Cu<sub>2</sub>S, lending further credence to the hypothesis that CuFeS<sub>2</sub> is decomposed and trivalent Fe is selectively reduced while most Cu, Fe, and S are removed during leaching. Increasing the FeCl<sub>3</sub> concentration also leads to an increase in the MoO<sub>2</sub> production, likely due to the decreased pH (Fig. 3). While no specification exists for an upper limit to the MoO<sub>2</sub> content, it is reasonable to assume that it should be minimized. An optimum must be struck between copper removal and MoS<sub>2</sub> conversion to MoO<sub>2</sub>. Fig. 3 demonstrates that the potential

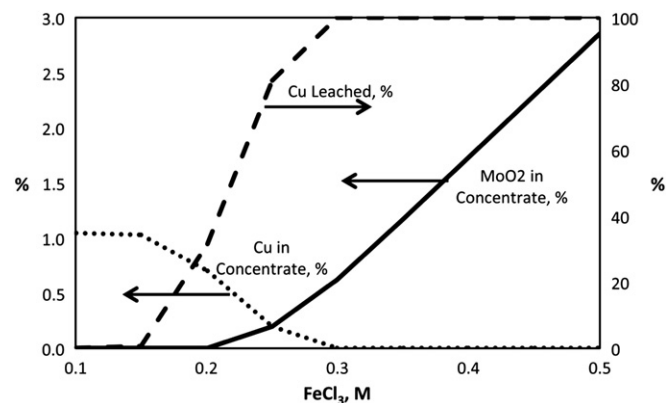


Fig. 2. Effect on CuFeS<sub>2</sub> leaching with 0.5 M HCl and varied FeCl<sub>3</sub> concentration; % MoO<sub>2</sub> in concentrate (solid), % Cu in concentrate (dot), % Cu leached (dash).

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