



## Fluoride Precipitation of Cu Over Fe in a Selected pH Window

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### ABSTRACT

Fe is an impurity in most leach liquors. Its coexistence with copper in leaching solution of chalcopyrite (CuFeS<sub>2</sub>) which is the most important mineral of copper creates major extraction problems. Hydrochloric acid dissolves both copper and iron during chloride leaching of this mineral. Separation of Fe from Cu is thus necessary to obtain pure copper. This paper presents a novel method for precipitation of Cu over Fe from mixed chloride acidic liquors. Hydrofluoric acid is used as the major unraveling agent. Kinetic studies show that a second-order CuCl<sub>2</sub> precipitation reaction with a chemical rate constant of  $k = 0.416$  L/mol prevails the process at the room temperature. For validation of the results, precipitate characterization by x-ray fluorescence (XRF) and x-ray diffraction (XRD) and solution analysis by atomic absorption spectrometry (AAS) are performed. Nitrogen presence is shown to help separation of iron from copper. The optimum value of pH (1.09) is achieved when nitrogen helps parting of 99 % iron II ions in the solution and sole deposition of copper II chloride precipitate.

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## 1. INTRODUCTION

Copper as a much-demanded metal [1] can be extracted by both pyrometallurgical [2-4] and hydrometallurgical ways [5, 6]. Within 30 years, the demand for copper production is predicted to raise three times more than the current amount [7]. Due to the environmental and energy limitations [8, 9], hydrometallurgy of copper has attracted much attention. It is also more economical and applicable to the units with lower capability [10]. Although traditional leaching is of much interest yet, biological and chemical processes have been given full consideration during recent years [11, 12]. Chalcopyrite chemical dissolution is a widely performed process utilizing sulfuric, nitric and hydrochloric acids. Oxidative dissolution of chalcopyrite at ambient temperature is slow [13] and subject to passivation [14], posing a challenge for development of leaching application. Chloride is, however, a well-known chemical enhancer for leaching of the most sulfidic substances [15].

Chloride leaching is both simple and economically feasible. However, safety precautions must be taken into consideration. Many works have been done to obtain the appropriate conditions [16-23]. Kinnunen et al. [24] have

studied the effect of chloride ions on chalcopyrite in biologically-produced ferric sulfate solutions. Sato et al. [11] have studied the effect of silver chloride on the bioleaching of chalcopyrite concentrate. Leaching of chalcopyrite in acidic ferric chloride has been reported by Al-Harashsheh et al. [18]. Sodium chloride has shown a positive effect on chalcopyrite dissolution resulting enhancement of copper extraction [25-27]. It has been shown that chalcopyrite leaching rates are faster with Fe (III)-chloride than with Fe (III)-sulfate [28]. Formation of a highly porous sulfur layer adjacent to the chloride solution has caused this faster rate [29, 30]. Previous authors have studied the mechanism of chalcopyrite leaching in hydrochloric acid solution [27]. They have analyzed solid residues by SEM, EPMA, Raman spectroscopy and XRD [27]. O'Malley et al. [31] have studied the leaching of CuFeS<sub>2</sub> by aqueous FeCl<sub>3</sub>, HCl, and NaCl. Habashi et al. [32] have compared oxidation behaviors of chalcopyrite in HCl and H<sub>2</sub>SO<sub>4</sub>.

Leaching of chalcopyrite results in the entrance of unwanted Fe<sup>2+</sup> ions into the dissolution product; because, the largest metallic impurity of copper ores is iron [33-36]. Separation of Fe from Cu is a time-consuming and

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expensive process requiring costly organic solutions. LIX 64N has been used in copper L/SX/EW technology, as is reported in the literature [36]. Finding a simple, inexpensive and fast way for the selective separation of Fe from Cu is still a desirable achievement that deserves extended research. This work is devoted to this purpose by looking through kinetics of precipitation of copper II chloride over Fe in a selected pH window by HF. Iron ions remain in the solution in the form of iron (II) fluoride. Copper (II) fluoride can then be used to synthesize fluoroaromatics substances [37]. Fluoride-based copper (II) catalysts are also usable in enantioselective hydrosilylation of ketones in aerobic conditions. Stainless steel cathode and platinum anode can be used for electrowinning of iron from fluoride solution through an autonomous process, such as the one studied by Mostad et al. [7]. The result can be thought of as an alternative to the well-established method of SX with LIX reagents [38], or even the old-fashioned copper cementation process.

## 2. MATERIALS METHOD

Analytical grade copper (II) and iron (II) chlorides were purchased from Merck, Germany. Hydrofluoric acid was purchased from Osloub Sanat Co., Iran. Nitrogen gas was also purchased from Sepehr Gas Nitrogen Co., Iran. Commercial chalcopryrite of Sarcheshme Copper Complex, Kerman, Iran was used to prepare industrial leaching solution.

As fluoride ion reacts with silica, PVC beakers were used for holding and transfer of HF. The solutions were diluted to levels acceptable for the atomic absorption spectrometer. Copper (II) and iron (II) chlorides were used to prepare synthetic chloride solutions.

Mixtures of copper (II) chloride and iron (II) chloride were stirred for 2 min. HF was then added and stirred until precipitation occurred. The deposits were then filtered and the pH of the solution was measured. The deposit was dried and then weighed. For phase detection, x-ray fluorescence and x-ray diffraction were performed. Concentrations of both copper and iron ions in the solution were measured by atomic absorption. Optimum pH for fastest precipitation and thus separation was obtained.

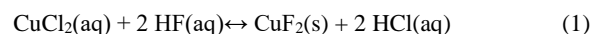
Experiments were repeated in the presence of nitrogen to find out the effect on N<sub>2</sub> on oxidation of iron (II) to iron (III). Effect of time on the proceeding of the reactions was studied by sampling at t = 2, 5, 10, 12, 15, 20, 25, 30, 35, 40 s after the start of the reaction. Kinetics of deposition of copper (II) fluoride was investigated. Liquid samples taken from the leaching solution were analyzed by atomic absorption spectrometer. Precipitates were characterized by x-ray fluorescence and x-ray diffraction. Thermodynamics and kinetics of the

reactions were studied by the standard free energy evaluations and conversion-time curve fitting to the established kinetic models available [39, 40].

## 3. RESULTS AND DISCUSSION

Table 1 shows the x-ray fluorescence results of the chalcopryrite powder used in this research. The data shows that the iron content of the sample is even higher than its copper concentration. The x-ray diffraction pattern of the precipitated powder is illustrated in Figure 1. The x-ray pattern indicates that a large amount of copper (II) fluoride together with a small amount of iron (III) fluoride with cubic crystal structure are present in the deposited solid phase.

Deposition of copper (II) fluoride can be projected according to the following reaction:



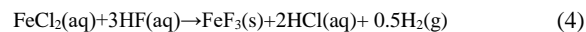
As iron (III) fluoride is insoluble, it would precipitate due to oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> according to the following unfavorable reaction:



Because of the acidic environment, cathodic H<sup>+</sup> reduction may facilitate the above reaction:

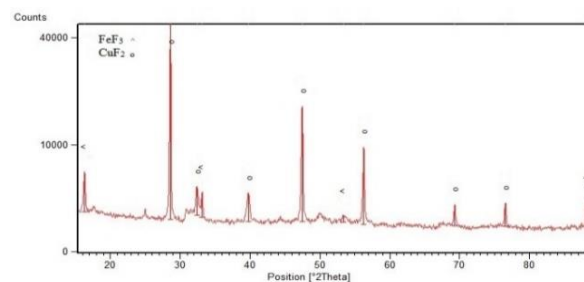


Combination of reactions (2) and (3) resulted in the deposition of the iron (III) fluoride out of the solution:



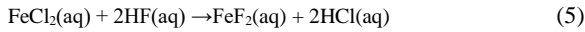
**TABLE 1.** XRF results of an industrial chalcopryrite powder

Compound	wt%	Compound	wt%	Compound	wt%
Na <sub>2</sub> O	8.0	MgO	1.5	Al <sub>2</sub> O <sub>3</sub>	1.5
SiO <sub>2</sub>	4.5	S	17.3	K <sub>2</sub> O	0.32
CaO	0.48	TiO <sub>2</sub>	0.16	Fe	15.7
Cu	13	ZnO	0.8	As <sub>2</sub> O <sub>3</sub>	0.24



**Figure 1.** XRD pattern of the deposited powder at pH = 1.83 and T = 298 K

High H<sub>2</sub> partial pressure, of course, can reverse the above unfavorable reaction. Utilization of hydrogen is, however, economically and practically unfeasible. Slow dissociation of HF is a simply done favorable phenomenon helping to succeed in the ionic separation. Based on literature, hydrofluoric dissociation and release of H<sup>+</sup> in water is not a fast process [41]. For iron ions to remain in the solution, the following is the favorable helpful reaction:



For the best separation of copper from iron, we try to minimize reaction (4) and maximize reactions (1) and (5) by controlling the pH of the solution.

Increasing H<sup>+</sup> ions causes progress of reaction (4). On the other hand, lack of H<sup>+</sup> ions inhibits the progress of reactions (1) and (5). Lack of H<sup>+</sup> ions means lack of hydrofluoric acid. Therefore, there is an optimum pH for the process.

Figure 2 shows the presence of copper and iron ions in the solution. Optimum pH is that which maximizes iron presence in the solution with heaviest copper precipitate. From Figure 2, the optimum pH is 1.09. In this pH, 99.9% of iron remains in the solution with 88.8% of copper going to the solid precipitate. Nitrogen gas can keep Fe<sup>2+</sup> ions far from the hydrogen ions. It, therefore, inhibits reaction (4) from quick occurrence. Figure 3 shows that nitrogen increases remaining of iron ions in the solution. Nitrogen atmosphere enhances efficiency up to 8%, although near to the optimized pH, the effect of nitrogen gas is negligible due to the higher stability of Fe<sup>2+</sup> ions in the solution.

Figure 4 explains the changes of the copper (II) fluoride content of the solution with time. As it is seen, it takes 12 s to reach the highest precipitation with the lowest remained copper in the leaching solution. Fractional conversion X of the reactants of reaction (5) is defined as follows:

$$X_A = (C^0_A - C_A) / C^0_A \quad (6)$$

In which C<sup>0</sup><sub>A</sub> is the initial concentration and C<sub>A</sub> is the concentration of the reactant at time t. Table 2 indicates partial conversions of copper II and HF in the solution.

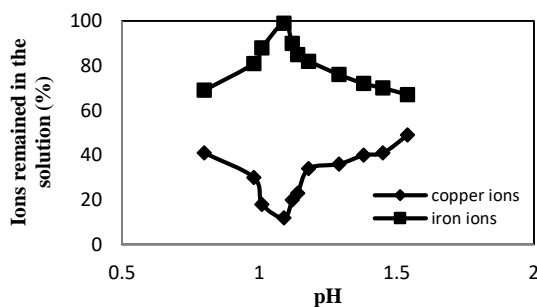


Figure 2. Solution ions content as a function of pH

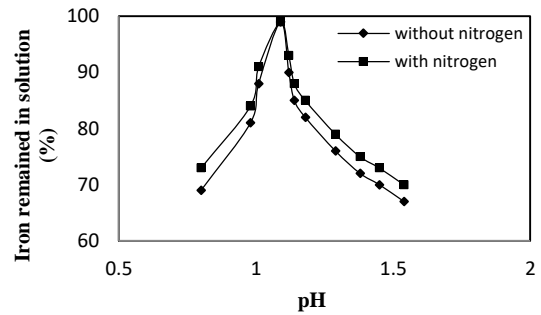


Figure 3. Effect of nitrogen on iron ions remained in the solution

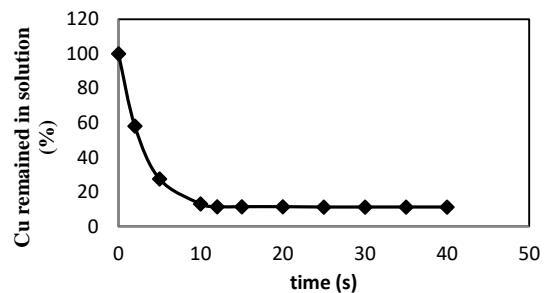


Figure 4. Changes of copper (II) chloride content in the solution for pH = 1.09 at 298 K with time

Applying kinetic model calculations [40], one can prove that the reaction (5) is a complex reaction with a total order of 2 as approved by the following procedure:

$$C_{\text{CuCl}_2} = C^0_{\text{CuCl}_2}(1 - X_{\text{CuCl}_2}) \quad (7)$$

Definition of the rate equation based on an assumed second order mechanism is:

$$-d(C_{\text{CuCl}_2})/dt = k C^0_{\text{CuCl}_2}(1 - X_{\text{CuCl}_2}) \times (C^0_{\text{HF}} - C^0_{\text{HF}} X_{\text{HF}}) \quad (8)$$

In which k is the rate constant and M is defined as follows:

$$M = C^0_{\text{HF}} / C^0_{\text{CuCl}_2} \quad (9)$$

The value of M in this study is selected to be equal to 2.266.

TABLE 2. Changes of concentration and fractional conversion for CuCl<sub>2</sub> and HF with the reaction time

t (s)	C <sub>CuCl<sub>2</sub></sub>	C <sub>HF</sub>	X <sub>CuCl<sub>2</sub></sub>	X <sub>HF</sub>	ln $\left( \frac{M - 2X_{\text{CuCl}_2}}{M(1 - X_{\text{CuCl}_2})} \right)$
0	0.5	1.133	0	0	0
2	0.28996	0.84304	0.42009	0.37077	0.42134
5	0.13688	0.99612	0.72624	0.64099	1.071228
10	0.06507	1.06794	0.86987	0.76776	1.76394
12	0.05697	1.07604	0.88607	0.78206	1.89096

As consumption of copper (II) chloride is half the consumption of hydrofluoric acid, we can write:

$$C_{\text{HF}}^0 X_{\text{HF}} = 2C_{\text{CuCl}_2}^0 X_{\text{CuCl}_2} \quad (10)$$

Substituting Equations (7), (9) and (10) into Equation (8), one can obtain:

$$dX_{\text{CuCl}_2}/dt = k C_{\text{CuCl}_2}^0 (1-X_{\text{CuCl}_2})(M - 2X_{\text{CuCl}_2}) \quad (11)$$

Equation (11) is the regularized of Equation (7) by the following equation:

$$\frac{dX_{\text{CuCl}_2}}{(1-X_{\text{CuCl}_2})(M-2X_{\text{CuCl}_2})} = k C_{\text{CuCl}_2}^0 dt \quad (12)$$

Integration of Equation (12) yields [38]:

$$\ln \left[ \frac{M-2X_{\text{CuCl}_2}}{M(1-X_{\text{CuCl}_2})} \right] = k C_{\text{CuCl}_2}^0 (M-2) t \quad (13)$$

In order to assess fitness of the proposed mechanism, we can plot  $\ln \left( \frac{M-2X_{\text{CuCl}_2}}{M(1-X_{\text{CuCl}_2})} \right)$  versus  $t$ . The result is shown in Figure 5 which shows a good fitness with a straight line of constant slope, as expected.

The slope of the straight line of Figure 5 is as follows:

$$k C_{\text{CuCl}_2}^0 (M-2) = 0.0553 \quad (14)$$

From the slope, the rate constant of the reaction (5) is obtained. Inserting  $M=2.266$  and  $C_{\text{CuCl}_2}^0 = 0.5$  mol/L into Equation (14), the value of the rate constant for the reaction (5) is obtained:

$$k = 0.4158 \text{ L/mol. s} \quad (15)$$

#### 4. SAFETY PRECAUTIONS

Both HF and HCl have corrosive effects on human tissue, potentially damaging respiratory organs, eyes, skin, and intestines. HF is a contact poison with un-noticed short-time effects. Skin burns may appear long-time after physical contact with HF. All leaching/separation practices must thus be done under a well-ventilated hood or inside well-controlled ventilated chambers with hands, eyes and other body parts protected with anti-acid safety

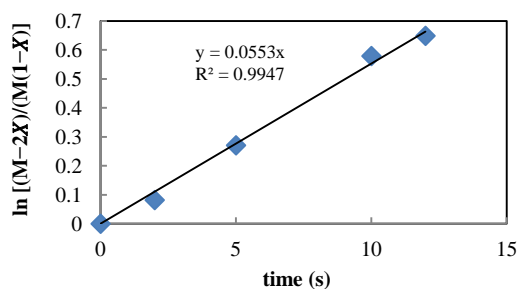


Figure 5. Plot of  $\ln \left( \frac{M-2X_{\text{CuCl}_2}}{M(1-X_{\text{CuCl}_2})} \right)$  versus time

covers. Safety regulations and measures are well established and fully documented for these acids because they are widely used in the production of organic or inorganic fluorine compounds, in the treatment of metals (aluminum, steel), glass and crystal (etching and polishing), in the petroleum industry (refining), in the electronics industry for the surface treatment of electronic components and in biological staining.

#### 5. CONCLUSIONS

Iron is the major impurity of copper almost in all natural resources. To fulfill the environmental limitations, reduction of energy consumption, and improving the economics of the production, the hydrometallurgical route was chosen in this research to part copper from iron. A simple, straightforward procedure was adopted to successfully attain separation of copper ions from chalcopyrite leaching solution through deposition of copper (II) fluoride. The separation reaction was found to be 1<sup>st</sup> order with respect to both  $\text{CuCl}_2$  and HF. The overall order of the separation reaction was two with a rate constant of  $0.4158 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ . An optimum value of pH for the highest departing of copper from ion was 1.09 when nitrogen gas was used to shield iron from precipitation with copper. Careful usage of HCl and HF was crucial for the safe operation of the devised new process.

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Copper-Iron Separation

$CuF_2$  Deposition

Reaction Mechanism

آهن در بسیاری از محلولهای لیچینگ وجود دارد. همزیستی آهن با مس در محلول لیچینگ کالکوپرایت ( $CuFeS_2$ ) که مهمترین ماده معدنی مس است، باعث ایجاد مشکلات عدیده‌ای در فرایند استخراج می‌شود. زیرا اسید هیدروکلریک مورد استفاده در لیچینگ کلریدی کالکوپرایت، هر دو عنصر مس و آهن را حل می‌کند. بنابراین برای تهیه مس خالص، لازم است  $Fe$  از  $Cu$  جدا شود. این مقاله روش جدیدی برای رسوب دادن  $Cu$  در برابر  $Fe$  از محلول اسیدی حاوی کلریدها ارائه می‌دهد. در این تحقیق، اسید هیدروفلوئوریک به عنوان عامل اصلی جداسازی آهن از مس مورد استفاده قرار می‌گیرد. مطالعات سینتیکی نشان می‌دهد که راسب شدن  $CuCl_2$  طبق یک واکنش درجه دو با ثابت سرعت  $k = 0.416 \text{ L/mol}$  در دمای اتاق اتفاق می‌افتد. برای اعتبار سنجی نتایج، مشخصه رسوب توسط اشعه ماوراء بنفش (XRF) و پراش اشعه ایکس (XRD) و تجزیه و تحلیل با اسپکترومتر جذب اتمی (ABS) انجام شده که نشان می‌دهد که حضور نیتروژن، جداسازی آهن از مس را تسهیل می‌کند. مقدار pH بهینه (1.09) موقعی به دست می‌آید که نیتروژن با جدایش 49٪ یون آهن II موجود در محلول، باعث رسوب همه کلرید مس II و بدین ترتیب جدایش تقریباً کامل دو عنصر می‌شود.

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