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Synergistic effects of ferric sulfate addition and mechanical activation on leaching of Sarcheshmeh copper sulfide concentrate

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ABSTRACT

In this paper, the leaching of a sulfide concentrate, from "Sarcheshmeh Copper Complex", by sulfuric acid is studied. The influences of sulfuric acid concentration and leaching temperature were scrutinized to optimize the processing parameters and to disclose the kinetics of the extraction process. The leaching rate of copper was not significantly improved with enhancing the temperature and concentration of sulfuric acid. The formation of elemental sulfur was found as a reducer of the leaching rate. Only ~70% of copper was extracted by adding 1M ferric sulfate as the oxidant agent, as well as increasing the leaching temperature up to 85 °C. By leaching the mechanically activated concentrate in $Fe_2(SO_4)_3$-doped H_2SO_4 at 85 °C, the amount of extracted copper was ~90% after 180 min. The experimental results were excellently fitted with the diffusion-controlled kinetic model as the activation energy of ~27 kJ/mol was estimated. ©2021 JCC Research Group.

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1. Introduction

Copper mainly exists with other metals in the form of complex sulfide ores. Such minerals can be detached from each other through the flotation process and processed via pyrometallurgical routes [1–4]. Although employing the pyrometallurgical routes is not environmentally attractive due to the production of significant SO_2; however, nearly 85% of the universal Cu is obtained by such processes [5, 6]. Complex sulfide concentrates such as chalcopyrite ($CuFeS_2$) can be treated by hydrometallurgical routes, which not only lead to enhanced copper extraction but also result in decreased air pollution hazards [7–12]. Chalcopyrite, as the main copious Cu sulfide mineral, is the best refractory Cu ore concerning chemical and bioleaching. Compared to the other metallic sulfides, the chalcopyrite can leach superbly at lower redox potential [13–16].

Because of the togetherness of chalcopyrite and pyrite in nature, a new galvanically-assisted process for chalcopyrite leaching has been introduced as the copper concentrate is leached under atmospheric pressure in the existence of pyrite in a ferric-ferrous sulfate solution [17–19]. Pyrite can be added as a catalyst to boost the leaching rate of Cu concentrate through forming a galvanic cell that intensifies the Cu leaching yield and rate [20]. However, recent works mention that ferric ion plays twofold roles as an oxidizing representative and responsible for chalcopyrite passivation [21, 22]. Various biological and chemical leaching processes have been developed to conquer the chalcopyrite passivation [23–25].

The influences of solution concentration, temperature, particle size, and stirring speed, as well as the kinetics of reaction were determined for the chalcopyrite leaching in sulfuric acid by sodium nitrate. Elemental sulfur was formed during the leaching process as an inhibitor of the leaching rate [26–28]. The influences of ferrous ions on oxidation of chalcopyrite with ferric ion in solutions of sulfuric acid were studied. The ferrous ion enhances the chalcopyrite oxidation beside the high-concentrated cupric ion [29, 30]. Combined chloride–sulfate leaching of chalcopyrite was also investigated, and excellent leaching kinetics was achieved for solutions containing chloride via promoting the formation of porous sulfur product and allowing the dissolution reaction to progress better [31–34].

In this research work, the leaching of Sarcheshmeh copper sulfide concentrate in sulfuric acid was studied. To improve the leaching process, the influences of some variables, including the processing temperature and preliminary acid concentration, were investigated. Moreover, the synergistic effects of ferric sulfate addition as an oxidant agent and the mechanical activation as a pre-leaching treatment were scrutinized.

2. Experimental procedure

2.1. Materials

The copper sulfide concentrate with the mean particle size of 120±30 µm was prepared from the "Sarcheshmeh Copper Complex", the world 2nd largest Cu deposit located in Kerman (Iran), was used in this research work. The mineralogical and chemical specifications of this material are

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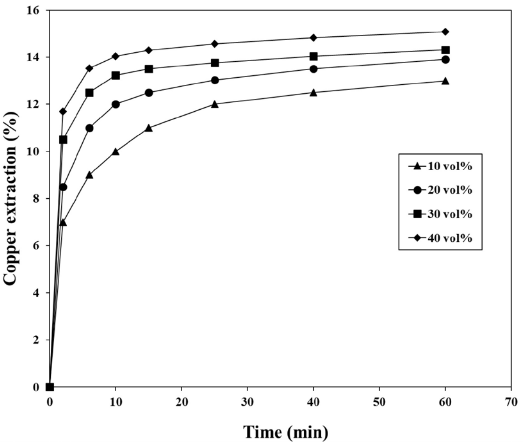

Fig. 1. Role of H_2SO_4 concentration on Cu extraction (stirring speed 400 rpm, particle size 120±30 µm, solid/liquid ratio 1/40, and temperature 25 °C).

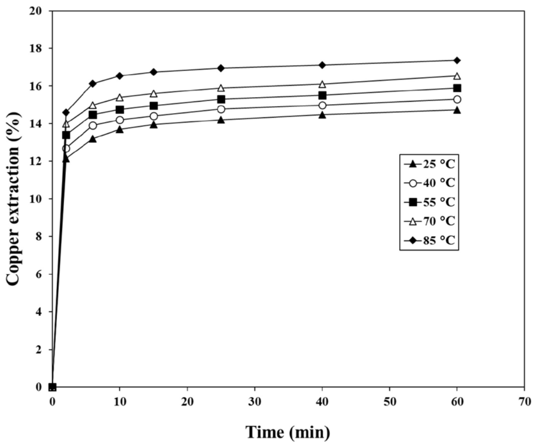

Fig. 2. Role of temperature on Cu extraction (stirring speed 400 rpm, particle size 120±30 µm, solid/liquid ratio 1/40 and 40 vol% H_2SO_4).

presented in Tables 1 and 2, respectively.

2.2. Methods

All leaching tests were performed on a magnetic stirrer in a 500-ml vessel supplied, a thermometer, a condenser, a funnel for adding the concentrate as well as a sampling device. Such a setup enables heating at a fixed temperature. The predetermined contents of commercially pure sulfuric acid (H_2SO_4) and in some experiments, Merck ferric sulfate ($Fe_2(SO_4)_3$) were introduced to the vessel and warmed up to the designated temperature. The concentrations of H_2SO_4 and $Fe_2(SO_4)_3$ were in the range of 15–40 vol% and 1 M, respectively. The sulfide concentrate was added to the solution when the temperature reached, and the chemical reactions were started. An atomic absorption spectrometer (AAS3, Variant Co.) was carried out for chemical analysis. In this way, 5-ml solution samples were taken after appointed intervals and were immediately replaced with the distilled water. Leaching processes were performed with a solid/liquid ratio of 1/40, a stirring speed of 400 rpm, temperatures of 25 to 85 °C, and soaking times of 60 to 180 min.

3. Results and discussion

Primary experiments, not reported here, showed that Cu extraction boosts with decreasing the particle size of starting concentrate. The particle size of 120±30 µm and the solid to liquid ratio of 1/40 were determined as the optimum leaching conditions for this research work. It was found that smaller particles and lower solid to liquid ratios provide a larger contact area between copper sulfide concentrate and sulfuric acid. In addition, the concentrate dissolution enhanced with increasing the stirring rapidity to 400 rpm, but after that, the extraction efficiency was lessened. Therefore, to investigate the other leaching parameters, such as the sulfuric acid concentration and processing temperature, the values as mentioned earlier were selected.

3.1. Role of sulfuric acid concentration

The role of H_2SO_4 concentration (10, 20, 30, and 40 vol%) on the copper leaching was studied at 25 °C, the solid to liquid ratio of 1/40, and the stirring speed of 400 rpm. The copper extraction enhanced from 13% to 15.1% after 60 min, while the H_2SO_4 concentration was intensified from 10 vol% to 40 vol%. More copper extraction was not achievable maybe due to the elemental sulfur formation on the surface of concentrate particles [35, 36].

3.2. Role of temperature

Fig. 2 displays the role of temperature on the extraction of copper sulfide concentrate under the following conditions: solid/liquid ratio 1/40, 40 vol% H_2SO_4, and stirring speed 400 rpm. It seems that the temperature did not have a noticeable influence on the leaching progress because the difference between the percentage of extracted copper at the range of 25–85 °C is less than 4% at all times. At 25 °C, 14.7% copper was extracted after 60 min, increased to only 17.4% at 85 °C. However, at all temperatures tested, a marked deceleration in the leaching rate is seen after 10 min. Such an observation can be related to the elemental sulfur formation during the leaching, which was precipitated at the surface of the concentrate particle and acted as a preventer to hinder the chemical reaction between the sulfide particles and sulfuric acid. Therefore, it can be concluded that the temperature increasing up to 85 °C is not enough to improve the copper extraction in the H_2SO_4 medium because the sulfuric acid, without oxidant agents, cannot significantly react with the sulfide concentrate.

3.3. Role of temperature in the presence of ferric sulfate

The sulfuric acid could not act as an efficient solvent, even at higher temperatures; hence, it was necessary to use an oxidant agent for a better leaching process [21, 37, 38]. The influence of $Fe_2(SO_4)_3$ as an oxidant agent on the Cu extraction was studied in the solution, including 40 vol% H_2SO_4 at 25, 55, and 85 °C with solid/liquid ratio of 1/40, stirring speed of 400 rpm, and adding 1 M $Fe_2(SO_4)_3$. The outcomes displayed in Fig. 3 verifies that Cu extraction enhances with temperature increasing. After 180 min, the copper leaching progressed from 28.1% to 72.3% when the extraction temperature was increased from 25 to 85 °C. How-

Table 1.
Copper sulfide concentrate mineralogical specification

Mineral	$CuFeS_2$	Cu_2S	CuS	Balanced
Mass %	32	21	2.5	44.5

Table 2.
Copper sulfide concentrate chemical specification

Element	Cu	Fe	S	Balanced
Content (%)	30	24	31	15

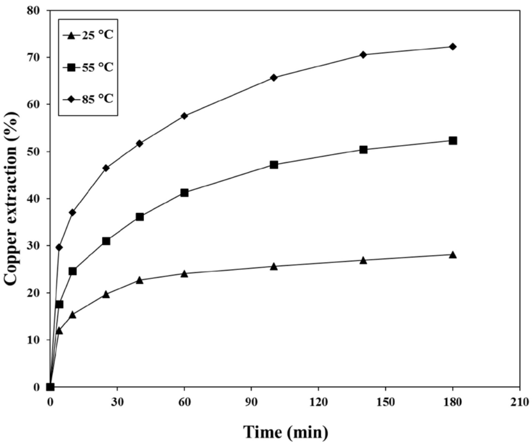

Fig. 3. FRole of temperature on copper extraction in the presence of 1M ferric sulfate (particle size 120±30 µm, solid/liquid ratio 1/40, stirring speed 400 rpm, and 40 vol% H_2SO_4).

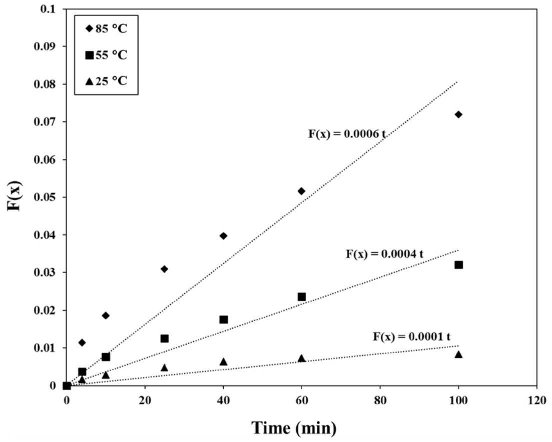

Fig. 5. The variations in F(x) with time at various temperatures based on the results reported in Fig. 3.

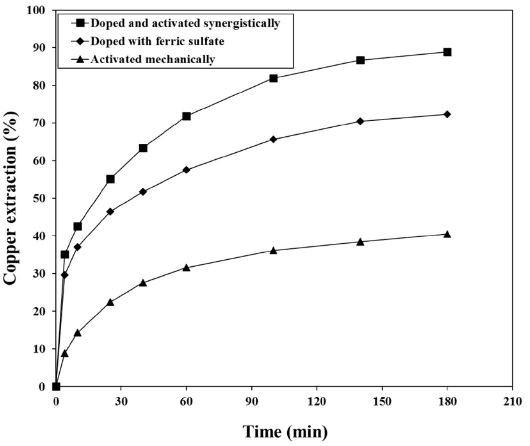

Fig. 4. Synergistic effects of ferric sulfate addition and mechanical activation on Cu extraction (particle size 120±30 µm, solid/liquid ratio 1/40, 40 vol% H2SO4, stirring speed 400 rpm and temperature 85 °C).

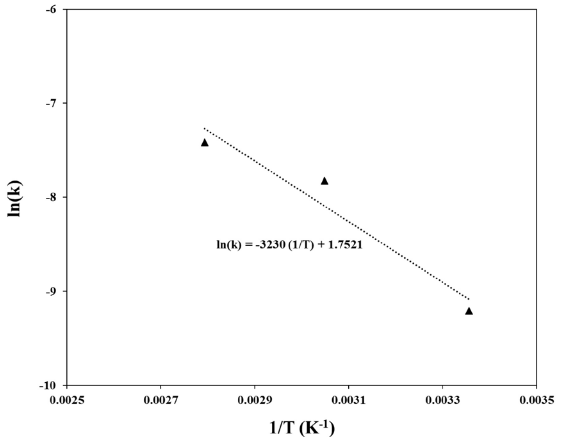

Fig. 6. Arrhenius plot for leaching of Cu concentrate.

ever, it seems that the sulfide concentrate cannot completely dissolve in $Fe_2(SO_4)_3$-doped H_2SO_4, even at an elevated temperature of 85 °C. Based on the Sarcheshmeh concentrate mineralogical data (Table 1) as well as according to the following chemical reactions between $Fe_2(SO_4)_3$ and the components of copper sulfide concentrate (Eqs. 1-3), the uncompleted dissolving can be attributed to the formation of sulfur on the surface of particles. The progress of such reactions leads to an inefficient contact between ferric sulfate and sulfide particles which hinders the full leaching of copper.

$$Fe_2(SO_4)_3 + Cu_2S = CuSO_4 + 2FeSO_4 + CuS \quad (1)$$

$$Fe_2(SO_4)_3 + CuS = 2FeSO_4 + CuSO_4 + S \quad (2)$$

$$2Fe_2(SO_4)_3 + CuFeS_2 = 5FeSO_4 + CuSO_4 + 2S \quad (3)$$

3.4. Synergistic effects of ferric sulfate and mechanical activation

The results of the previous section showed that by adding the oxidant agent as well as raising the leaching temperature, only ~70% of copper could be extracted from the sulfide concentrate. In this section, at first, the role of mechanical activation on the efficiency of copper concentrate leaching was studied. In this way, a mechanically activated concentrate was leached in the 40 vol% H_2SO_4 solution with a stirring speed of 400 rpm and a solid/liquid ratio of 1/40 at the temperature of 85 °C. As presented in Fig. 4, the amount of extracted copper after 60 min is 31.6%, approximately two times higher than that for the concentrate leached at the same conditions but without mechanical activating (17.4%, Fig. 2). This outcome verifies the positive role of the mechanical activation process on the enhancement of copper extraction. However, after 180 min leaching, even with the help of such a supportive process, the extracted copper did not exceed 40.5%.

In the previous section, it was discussed that in $Fe_2(SO_4)_3$-doped H_2SO_4 solvent, the copper leaching progressed to 72.3% at 85 °C after 180 min (Fig. 3). The results of such conditions are also repeated in Fig. 4 for a comparative approach. The extraction process was finally performed under a synergistic condition in which the mechanically activated copper concentrate was leached in the ferric sulfate doped medium. The results showed an enhancement in the percentage of copper extracted to 88.9% after 180 min leaching. It seems that by employing such technique, the surface area, surface reactivity, and surface microstructural modification led to a better reactivity between the copper concentrate and H_2SO_4 solvent, which has doped with $Fe_2(SO_4)_3$.

3.5. Leaching kinetics

Choosing a kinetic model for the experiments linearization reported in Fig. 3 was performed through the "shrinkage core model". Based on such a model, the experimental results approximated to the values of the following kinetic equation (Eq. 4); hence, this equation was used for the linearization of experimental data.

$$F(x) = 1 - \frac{2}{3}x - (1-x)^{2/3} = kt \qquad (4)$$

where x fraction of dissolved copper, k is constant (min^{-1}), and t is reaction time (min). The variations of F(x) with time at various temperatures are shown in Fig. 5. This kinetic model proposes a diffusion control mode as the dominant rate controller of the leaching process. Although, the leaching can be restricted by the surface chemical reactions in the primitive steps, it seems that with the progress of the elemental S on the surfaces of concentrate particles, the diffusion of the reactant through such layers will be the rate-controlling stage, as shown in Fig. 5.

To estimate the activation energy (E_a), the Arrhenius graph for the leaching of Cu concentrate in $Fe_2(SO_4)_3$-doped H_2SO_4 solution was achieved by drawing the value of the slope of the straight line in Fig. 5 versus ln(1/T) as displayed in Fig. 6. The amount of activation energy was evaluated ~27 kJ/mol, using Eq. 5: Arrhenius equation where k_0 is a constant, R is the universal gas constant, and T is the temperature, which shows that the leaching of copper concentrate is a diffusion-controlled process.

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \qquad (5)$$

4. Conclusions

The leaching process of sulfide concentrate from the Sarcheshmeh Copper Complex in Kerman province of Iran by ferric sulfate and sulfuric acid was studied. The following results were achieved:

1. The copper extraction enhanced from 13% to 15.1% after 60 min, when the H_2SO_4 concentration increased from 10 vol% to 40 vol%.
2. Increasing the sulfuric acid concentration and temperature did not lead to a remarkable enhancement in the amount of extracted copper.
3. More copper extraction was not achieved due to the formation of elemental S on the surfaces of concentrate particles.
4. By adding $Fe_2(SO_4)_3$ oxidant, the maximum leaching degree was only ~70% at 85 °C after 180 min.
5. By employing the mechanical activation trick and adding ferric sulfate to the solution, the amount of extracted copper reached ~ 90%.
6. The kinetic outcomes for the leaching process showed an excellent fit to the diffusion-controlled model, and ~27 kJ/mol was estimated as the activation energy.

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Conflict of interest

The authors declare that there is no conflict of interest.

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