

Article

Improvement of Copper Metal Leaching in Sulfuric Acid Solution by Simultaneous Use of Oxygen and Cupric Ions

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Abstract: A new concept for copper (Cu) metal leaching by the simultaneous use of cupric ions (Cu^{2+}) and oxygen (O_2) was proposed to improve Cu metal leaching in sulfuric acid. According to this concept, Cu^{2+} oxidizes Cu metal into cuprous ion (Cu^+), and O_2 oxidizes Cu^+ into Cu^{2+} . The improvement in Cu leaching efficiency from Cu metal was investigated experimentally in the sulfuric acid solution using Cu^{2+} and O_2 simultaneously. Furthermore, the result was compared with that for the sulfuric acid solution containing neither Cu^{2+} nor O_2 and with the sulfuric acid solution without Cu^{2+} and O_2 . When both Cu^{2+} and O_2 were used in the leaching solution, the leaching rate of Cu from Cu metal powder was higher than at other leaching conditions, and the leaching efficiency of Cu increased to more than 99.9% in 1 mol/L sulfuric acid solution at 400 rpm and 50 °C with $\leq 75 \mu\text{m}$ Cu metal powder, 1% pulp density, 10,000 mg/L initial Cu^{2+} concentration, and 100 cc/min O_2 introduction. These results indicated that the leaching of Cu from Cu metal could be accelerated by adding Cu^{2+} and O_2 in the sulfuric acid solution.

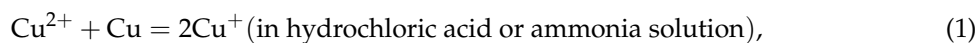
Keywords: copper; leaching; oxygen; cupric ion; sulfuric acid

1. Introduction

The International Copper Study Group (ICSG) reported that 33% of global copper use came from recycled copper in 2017 [1]. Although more than 70% of refined copper is produced by smelter [1,2], there have been many studies to recover copper from secondary sources such as printed circuit boards (PCBs) using hydrometallurgical ways, which have some advantages such as less gas emission and lower capital cost than pyrometallurgical processes [3–12]. Leaching is the first step of hydrometallurgical process for copper recovery from secondary sources, where copper metal must be oxidized into copper ion such as cuprous ion (Cu^+) or cupric ion (Cu^{2+}) because copper in the secondary sources is present as elemental copper [3,4].

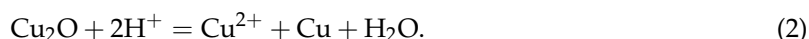
The standard reduction potential of copper is +0.34 V ($\text{Cu}^{2+} + 2\text{e} = \text{Cu}$) [13], which is higher than that of hydrogen (0 V); therefore, copper cannot be oxidized by sulfuric acid. Hence, strong oxidants such as nitric acid, hydrogen peroxide, and ferric ion have been investigated to oxidize copper for the leaching of copper [3,14–18]. These oxidants have the following disadvantages: NO_x gas could be generated from nitric acid leaching [3]; hydrogen peroxide has been found to be unstable and expensive [3,14–16]; and when Fe^{3+} ion is used as an oxidant, an additional process after leaching is required to separate the Cu ion from Fe ions [17,18].

Cupric ions (Cu^{2+}) have been recognized as an alternative to the strong oxidants [4,19–21]. However, it was reported that the cupric ions can act as oxidants only in hydrochloric acid or ammonia solutions. The oxidation reaction can be summarized as follows [19,20]:



where the cuprous ion (Cu^+) plays a key role in the reaction because the reaction cannot proceed without Cu^+ . Generally, Cu^+ ions can exist as complex ions in hydrochloric acid or ammonia solutions. These ions are unstable in a sulfuric acid solution; hence, it is understood that the reaction represented by Equation (1) is unlikely to occur in a sulfuric acid solution.

In conventional studies [22–24], the instability of cuprous ions in a sulfuric acid solution has been reported by examining the leaching behavior of Cu from cuprous oxide (Cu_2O). When Cu_2O was leached in a sulfuric acid solution under anoxic conditions, the Cu^+ ions dissolved out from Cu_2O , but they were immediately transformed into Cu^{2+} ions and Cu due to their instability. The transformation reaction can be represented as follows [22–24]:



As shown in Figure 1a, under anoxic conditions, when one of the two Cu^+ ions, which are dissolved out from Cu_2O , oxidizes to cupric ion (Cu^{2+}) by losing an electron, the other Cu^+ ion gains the electron and is transformed into elemental copper (Cu^0). Thus, a balanced chemical reaction occurs. Figure 2 shows the XRD data of Cu_2O reagents (before leaching) and leaching residue (after leaching), respectively, where Cu metal peaks were observed after leaching.

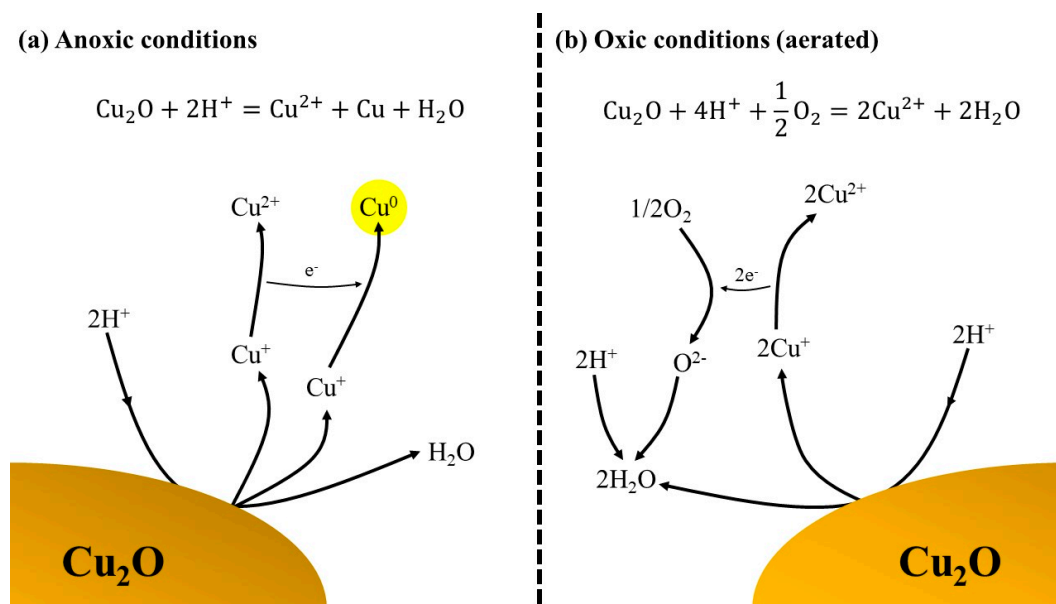


Figure 1. Leaching behavior of copper from Cu_2O in sulfuric acid leaching under (a) anoxic and (b) aerated conditions.

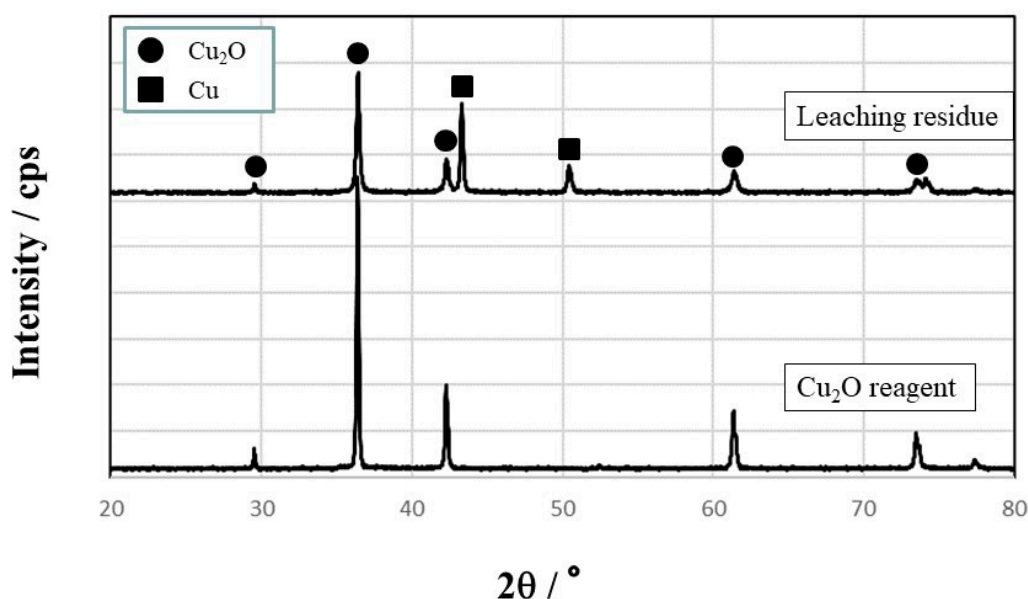
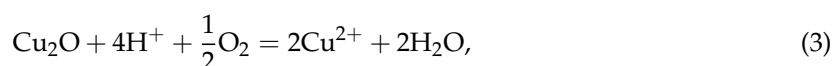


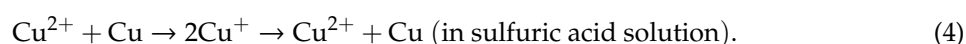
Figure 2. XRD peaks of leaching residue and Cu_2O reagent. Leaching conditions; 1 mol/L sulfuric acid without aeration, 50 °C, 400 rpm, 2% pulp density [23].

In the previous study [23], the leaching tests with and without oxidants (1000 cc/min air) were performed to investigate the leaching behaviors of Cu from reagent Cu_2O in 1 mol/L sulfuric acid solution at 400 rpm and 30–90 °C with 2% pulp density. The leaching efficiency of Cu increased to 100% within 60 min with the aeration, while a lower leaching efficiency was observed without the introduction of air. The leaching with aeration was given by

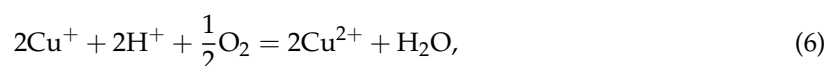
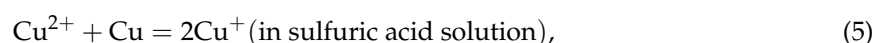


where oxygen in the air acts as an electron acceptor, as shown in Figure 1b. Thus, all the cuprous ions could be oxidized to cupric ions during Cu_2O leaching. Park et al. reported that the leaching efficiency of Cu from Cu_2O increased to 100% under aerated leaching conditions [23].

As discussed previously, due to the instability of the Cu^+ ions, it is understood that the reaction represented by Equation (1) is unlikely to occur in sulfuric acid. However, the behavior has not been investigated in detail. We assumed that the oxidation of copper metal by cupric ions has taken place in the sulfuric acid solution without oxygen, and the new concept of copper leaching is shown in Figure 3b. Although copper metal could be oxidized by the cupric ion in sulfuric acid as shown in Equation (1), the Cu^+ ions oxidize to Cu^{2+} ions or reduce to Cu^0 , as shown in Figure 3a. This is because the Cu^+ ions of the reaction product are unstable in sulfuric acid. These reactions can be summarized by the following equation:



Equation (4) indicates that even if the Cu^{2+} ions could oxidize Cu metal in the sulfuric acid solution, it may appear that no reactions have occurred because the Cu^+ ions transform immediately into Cu^{2+} ions or Cu. As shown in Figure 3b, when oxygen is introduced into the system, the oxygen oxidizes the Cu^+ ions, which are generated by the oxidation of Cu metal by the Cu^{2+} ions. The reactions can be represented as follows:



where the Cu^+ ions act as an intermediate. Hence, the overall reaction can be rearranged as follows:

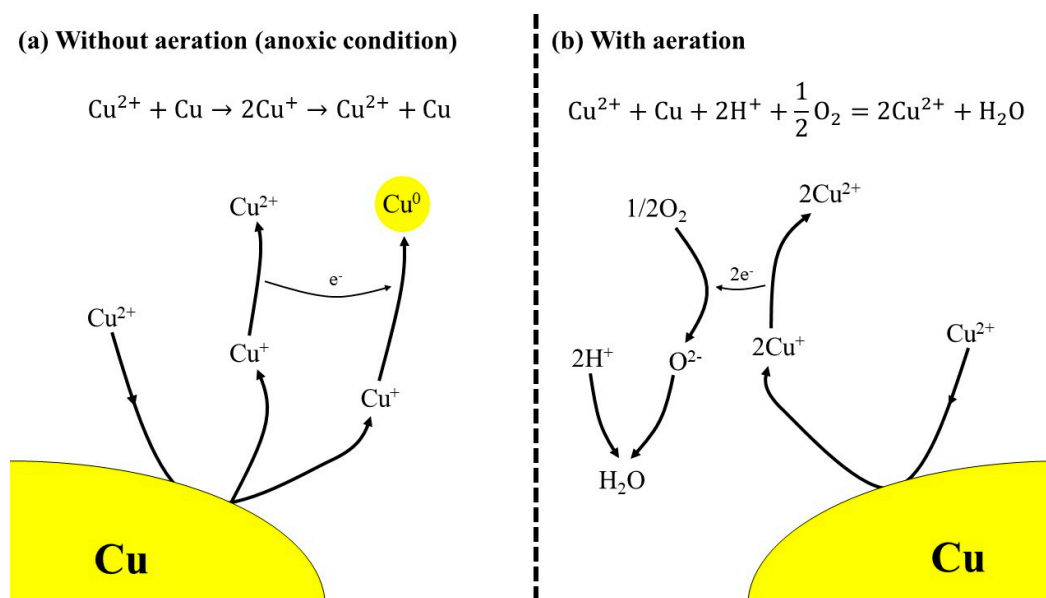
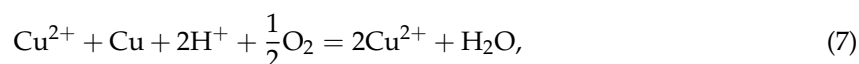


Figure 3. The proposed concept of leaching behavior of copper from Cu metal by Cu^{2+} ions in sulfuric acid leaching: (a) without aeration and (b) with aeration.

Equation (7) indicates that the combination of Cu^{2+} ions and O_2 could leach the Cu^{2+} ions from copper metal. However, the effects of the addition of the Cu^{2+} ions and introduction of oxygen on the enhancement of copper leaching have not been investigated in a sulfuric acid solution. Since oxygen has a relatively high standard redox potential to oxidize copper metal ($\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$, + 0.40 V) [13], only O_2 can oxidize copper and has been used in de-copperization from the anode slime. Therefore, in this study, four experimental conditions were compared to investigate the oxidation of copper metal powder in the sulfuric acid solution. These conditions were as follows: the addition of Cu^{2+} ions with the introduction of O_2 , the addition of Cu^{2+} ions with the introduction of N_2 , the introduction of O_2 without the addition of Cu^{2+} ions, and the introduction of N_2 without the addition of Cu^{2+} ions. Thus, the synergistic effect produced by using the Cu^{2+} ions and O_2 was investigated for copper metal leaching.

2. Materials and Methods

Two different sizes ($\leq 75 \mu\text{m}$ ($\geq 95\%$, Junsei Chemical Co., Ltd., Tokyo, Japan) and $150\text{--}420 \mu\text{m}$ (99.5% , Alfa Aesar Chemical Co., Ltd, Ward Hill, MA, USA)) of the copper metal powder were used in this study. For leaching tests, 1 mol/L sulfuric acid solutions with and without 10,000 mg/L Cu^{2+} were prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99.0%, Junsei Chemical Co., Ltd., Tokyo, Japan) in sulfuric acid ($\geq 95\%$, Junsei Chemical Co., Ltd., Tokyo, Japan) and distilled and deionized water. The solutions were transferred to a 500 cm^3 four-necked Pyrex glass reactor (Daihan Scientific Co., Ltd, Wonju, Korea) and the temperature of the solutions was maintained at $50 \text{ }^\circ\text{C}$ using a heating mantle. The reactor was fitted with a stirrer, gas inlet/outlet tubes, and a reflux condenser. In addition, 100 cc/min of O_2 , air and N_2 gas were introduced through the inlet tube during the leaching tests, and the purity of all gases is 99.99%. When the temperature of the solution was stabilized, 2 g of Cu metal powder was added into the solutions, and the solutions were withdrawn at designated times. The solutions were filtered with a $0.45 \mu\text{m}$ membrane filter and subsequently diluted with 5% HNO_3 for ICP-OES (inductively coupled plasma optical emission spectrometer, PerkinElmer, Inc. Waltham, MA, USA) analysis.

3. Results and Discussion

In Equations (5)–(7), the Cu^+ ions play a key role as an intermediate. However, it is difficult to detect the Cu^+ ions in the sulfuric acid solution due to their instability. Therefore, the improvement in copper metal leaching was verified experimentally in sulfuric acid solution by adding the Cu^{2+} ions and introducing O_2 . Four leaching conditions were used according to the addition of the Cu^{2+} ions and introduction of O_2 , and the leaching behavior of Cu from Cu metal was investigated.

Figure 4 shows the leaching behavior of Cu in 1 mol/L sulfuric acid solution at 50 °C and 400 rpm with 1% pulp density and $< 75 \mu\text{m}$ Cu metal powder. The leaching efficiencies of Cu increase rapidly when O_2 is introduced into the solution, while they increase gradually when N_2 is introduced into the solution. The leaching efficiency of Cu increases more rapidly in the case of the solutions containing 10,000 mg/L Cu^{2+} ions than in the case of the solutions not containing 10,000 mg/L Cu^{2+} ions. Moreover, the leaching efficiency of Cu increased to more than 99.9% within 60 min in the sulfuric acid solution containing 10,000 mg/L Cu^{2+} ions.

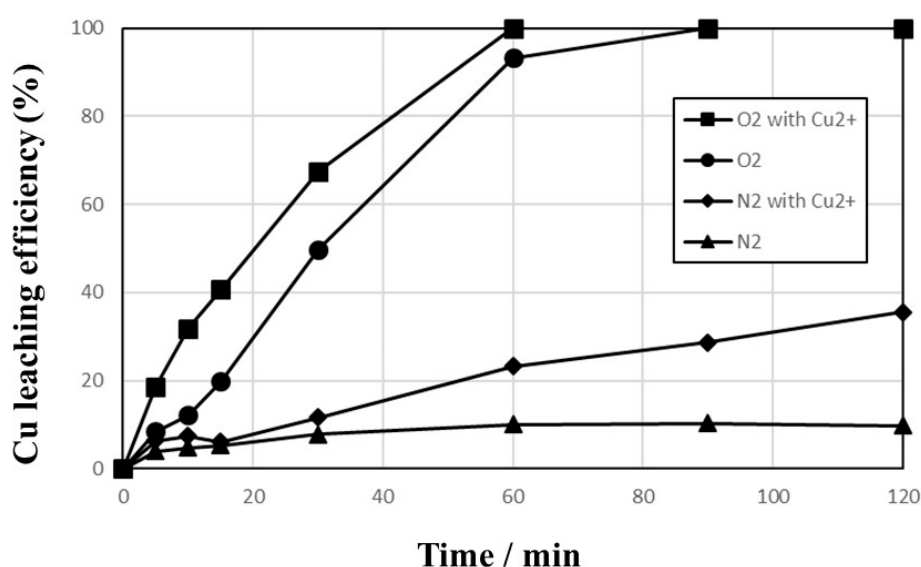


Figure 4. Leaching behaviors of Cu in 1 mol/L sulfuric acid solution at 50 °C and 400 rpm with 1% pulp density and $\leq 75 \mu\text{m}$ Cu metal powder.

Figure 5 shows the leaching behavior of Cu in 1 mol/L sulfuric acid solution at 50 °C and 400 rpm with 1% pulp density and 150–420 μm Cu metal powder. The leaching of Cu is slower with 150–420 μm than with 75 μm Cu metal powder, as observed after comparing Figures 4 and 5. When oxygen is introduced into the solution, the improvement in Cu metal leaching by adding the Cu^{2+} ions is remarkable, as shown in Figure 5. Further, the leaching efficiency of Cu in the solution containing 10,000 mg/L Cu^{2+} ions increases to 54.8% after 120 min, while that of the solution not containing 10,000 mg/L Cu^{2+} ions increases to 35.6%.

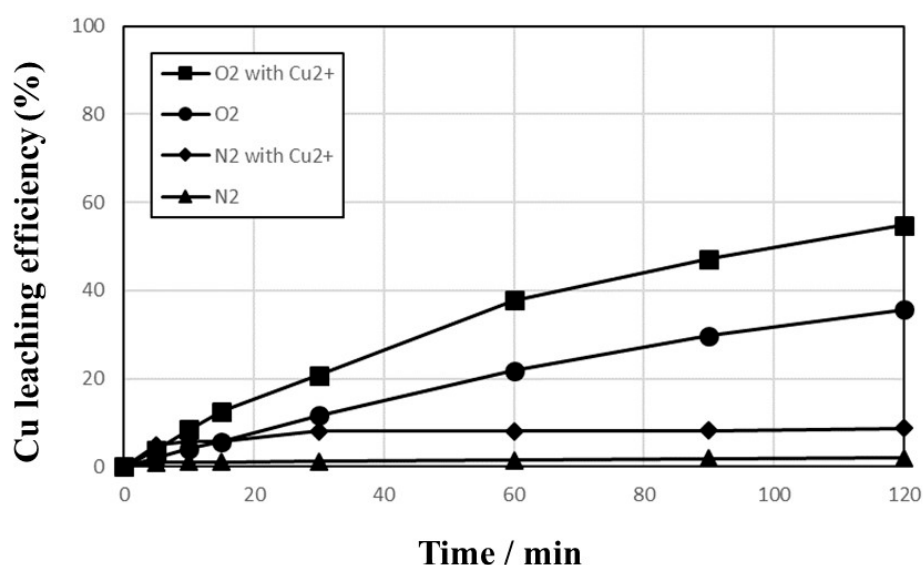


Figure 5. Leaching behaviors of Cu in 1 mol/L sulfuric acid solution at 50 °C and 400 rpm with 1% pulp density and 150–420 μm Cu powder.

In Figures 4 and 5, in the cases of N_2 gas introduction, the leaching efficiencies of Cu are lower than those with O_2 gas introduction. The leaching efficiencies with N_2 introduction and $<75 \mu\text{m}$ Cu metal powder increase to 9.8% and 35.5% without and with 10,000 mg/L Cu^{2+} ions, respectively, after 120 min. In the case of 150–420 μm Cu metal powder, the leaching efficiencies were 2.0% and 8.8% without and with 10,000 mg/L Cu^{2+} ions, respectively, after 120 min. Although Cu metal cannot be dissolved theoretically by sulfuric acid, the dissolution of Cu would result from the following two reasons. (1) The surface of Cu metal powder could be partially oxidized into Cu_2O as reported before [25]; thus, even sulfuric acid could dissolve the oxidized copper surface. Or, (2) a vortex could be formed during agitation; therefore, a small amount of air (oxygen), which was introduced into the leach solution, could act as an oxidant. Further study will be required to investigate what factors affect the leaching efficiency under the condition.

Figure 6 shows the leaching efficiencies of Cu with different gases such as O_2 , air, N_2 , and without gas introduction under the following conditions: 1 mol/L H_2SO_4 concentration, 400 rpm agitation speed, 50 °C temperature, 1% pulp density, $<75 \mu\text{m}$ -sized Cu metal powder, and 10,000 mg/L Cu^{2+} concentration. When 10,000 mg/L Cu^{2+} ions are added, the leaching efficiency increases to more than 99.9% in 60 min with 100 cc/min of O_2 introduction. In addition, the leaching efficiency increases to 98.1% after 120 min with 100 cc/min of air introduction. The oxygen in Equation (7) indicates the dissolved oxygen, and the leaching efficiency is higher with O_2 than with air because the partial pressure is higher during O_2 introduction. The leaching efficiency increases to 79.1% after 120 min without gas introduction because it is caused by the inflow of air due to vortex formation during agitation. The dissolution of Cu was suppressed by introducing N_2 gas to avoid O_2 inflow.

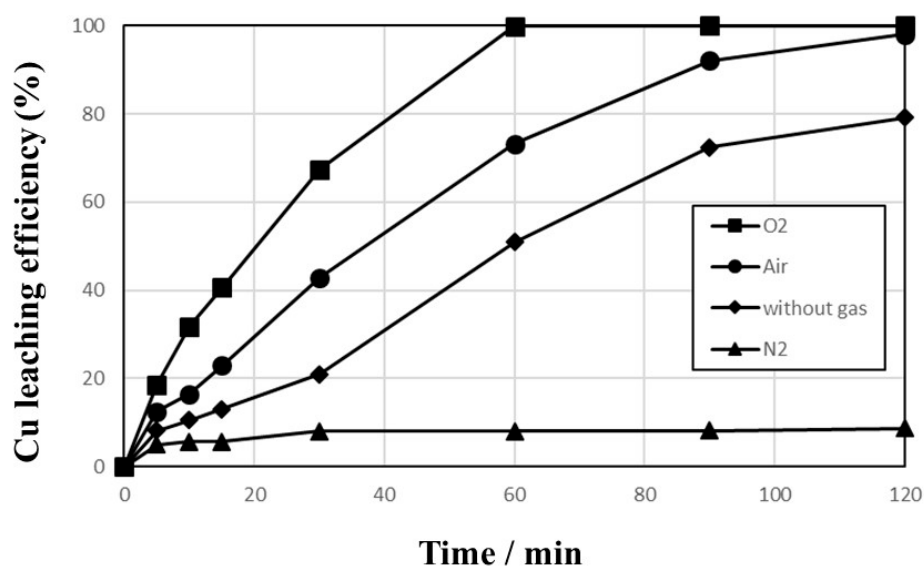


Figure 6. Effects of the introduction of gases on the leaching behaviors of Cu in 1 mol/L sulfuric acid solution at 400 rpm with 1% pulp density, $\leq 75 \mu\text{m}$ Cu powder, and 10,000 mg/L Cu^{2+} ions.

4. Conclusions

The leaching process of copper metal in sulfuric acid solution with both Cu^{2+} and O_2 was proposed to avoid the use of nitric acid or hydrochloric acid and the addition of oxidants such as Fe^{3+} for copper metal leaching. The leaching of Cu metal was enhanced by adding Cu^{2+} ions and introducing O_2 in the sulfuric acid solution; e.g. the leaching efficiency of Cu increased to more than 99.9% within 30 min in 1 mol/L sulfuric acid solution with 10,000 mg/L Cu^{2+} at 400 rpm with 1% pulp density, $< 75 \mu\text{m}$ particle size, and 100 cc/min O_2 . It was also observed that a smaller particle size increases the leaching efficiency of Cu. In this case, it is suggested that the added Cu^{2+} ions oxidize Cu metal into Cu^+ ions, and the O_2 introduced into the sulfuric acid solution further oxidizes the Cu^+ ions into the Cu^{2+} ions. The use of Cu^{2+} ions and O_2 is for Cu metal leaching would leave no impurity in solution after leaching.

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