Leaching of Copper from Malachite with Methane-sulfonic Acid

Qicheng FENG,1 Shuming WEN,1,* Wenjuan ZHAO,2 Cao LV1 and Xv BAI1

1State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, P.R. China
2Kunming Metallurgical Research Institute, Kunming 650031, P.R. China
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The process of leaching copper from malachite using methane-sulfonic acid (MSA) as an organic leaching reagent was investigated in this study. The effects of acid concentration, reaction temperature, particle size, and stirring speed on the copper leaching fraction were determined. Results indicated that leaching reagent concentration and reaction temperature exerted significant effects on copper extraction, whereas particle size and stirring speed exerted a relatively minor effect on the leaching rate. The kinetics of the dissolution process followed the shrinking core model, and a new kinetic model was found suitable to represent the rate-controlling step. The apparent activation energy of this process was determined to be 24.48 kJ/mol, and a semi-empirical rate equation was obtained to describe the process.

1. Introduction

As an important nonferrous metal, copper is widely applied in the electrical and electronics industries, the rolling industry, communication, aviation industries, and the chemical industry because of its excellent physical and chemical properties [1, 2]. In previous years, copper was primarily smelted from copper sulfide minerals after being separated from gangue minerals by beneficiation methods [3–5]. However, the recovery of copper by conventional pyrometallurgical techniques is associated with the undesirable emissions of harmful sulfur oxides into the atmosphere [6, 7]. Moreover, rapid economic and technical developments have resulted in an increasing demand for copper and gradual depletion of copper sulfide ores [8–9]. Thus, hydrometallurgy has been applied as an alternative method to extract copper metal from oxidized copper minerals to meet future demands.

Leaching is a key step in hydrometallurgical processes, and the selection of an appropriate leaching reagent is vital to the leaching efficiency. To date, several leaching agents have been used in copper hydrometallurgical processes, such as acids and alkaline media [10–15]. Inorganic acidic media, such as sulfuric acid, hydrochloric acid, nitric acid, have been commonly used to extract copper from feed materials. Given the increasingly strict environmental protection regulations with regard to sustainable development and certain disadvantages of inorganic acids present in the leaching process, organic acids such as citric, acetic and oxalic acids can be advantageous leaching agents. However, weak acidity is characteristic of organic acids, and their low boiling temperatures and instability restrict their industrial applications [2, 16–18]. Numerous studies on the extraction of copper from oxidized copper minerals using alkaline media, such as ammonia, ammonia/ammonium carbonate, ammonium chloride, ammonium sulfate,
and ammonium nitrate, have been conducted [19–21]. However, this technology suffers from the volatility of ammonia in aqueous solution, which significantly deteriorates the operation environment. Furthermore, the leaching equipment has been proven to be complicated and expensive to operate [20, 22–23]. Thus, efficient green leaching reagents for extracting copper from oxidized copper minerals need to be developed for the treatment of such ores.

Methanesulfonic acid (MSA) is an organic leaching reagent that can dissolve copper-bearing minerals through the formation of soluble copper methanesulfonate. Meanwhile, MSA has certain excellent properties, such as high conductivity, stability against volatilization and hydrolysis, and low corrosiveness and toxicity [24–26]. Besides, aqueous copper methanesulfonate can be directly used in electroplating and in the electronics industry. Thus, MSA is proposed for the extraction of copper from malachite, which is a common oxidized copper mineral.

Although a number of acidic and alkaline leaching reagents have been used to extract copper from malachite, and the corresponding leaching kinetic studies were carried out, no information on leaching malachite in MSA solutions and a corresponding kinetic study has been reported so far. Therefore, this study aimed to investigate the dissolution behavior of pure malachite using aqueous MSA solutions as leaching reagents to develop a kinetic model that is suitable for representing the rate-controlling step, and to obtain the kinetic parameters of this leaching process. The effects of parameters, such as MSA concentration, reaction temperature, particle size, and stirring speed, on the dissolution process of malachite were also evaluated.

2. Experimental

2.1 Materials and dissolution procedure

Pure malachite samples were obtained from the Dongchuan copper ore mine in Yunnan Province, China. The mineral samples were hand-ground in a mortar and then sieved using standard test sieves to produce the required particle sizes for the dissolution experiments. The chemical analysis results for the sample as shown in Table 1 revealed that the malachite contained 57.41% Cu, which indicated that the malachite samples were of high purity. The X-ray diffraction (XRD) pattern of samples which is shown in Figure 1 demonstrated that only malachite crystals were detected and the diffraction peaks of the samples were consistent with the values specified in the JCPDS card (No. 76-0660). All reagents used in this study were of analytical grade. Pure deionized water was used for all experiments.

Table 1. Chemical analysis results for the pure malachite sample.

<table>
<thead>
<tr>
<th>Component</th>
<th>Cu</th>
<th>O</th>
<th>C</th>
<th>Pb</th>
<th>Zn</th>
<th>Al</th>
<th>Ca</th>
<th>Fe</th>
<th>S</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (mass %)</td>
<td>57.41</td>
<td>36.75</td>
<td>5.62</td>
<td>0.04</td>
<td>0.07</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
</tbody>
</table>
All dissolution experiments were conducted in a laboratory apparatus which is composed of a 500 mL three-necked flask batch reactor, a digitally controlled mechanical stirrer, a condenser for preventing evaporation loss, a thermometer for temperature control and a thermostatically controlled water bath for heating. For each experiment, the solid/liquid ratio was kept constant at 1/100 g/mL, i.e., 5 g of malachite of the required particle size was stirred in 500 mL of freshly prepared MSA solutions of various concentrations and heated to the required temperature. A 5 mL portion of the resultant solution was accurately withdrawn at appropriate time intervals and was subjected to quantitative analysis for dissolved copper using an atomic absorption spectrophotometer. Thus, the amount of dissolved copper in the solution at each leaching time was determined. Then the copper leaching fraction \( x \) was calculated as follows:

\[
x = \frac{\text{mass of copper in the solution}}{\text{mass of copper in malachite samples}}.
\]

2.2 Dissolution principle

Malachite \((\text{Cu}_2(\text{OH})_2\text{CO}_3)\) can be dissolved in MSA \((\text{CH}_3\text{SO}_3\text{H})\) solution because a water-soluble salt is formed. The reactions between malachite and MSA may be expressed by equations (1) and (2).

\[
2\text{CH}_3\text{SO}_3\text{H}^{(\text{aq})} \rightarrow 2\text{CH}_3\text{SO}_3^{3(\text{aq})} + 2\text{H}^+(\text{aq}) \\
\text{Cu}_2(\text{OH})_2\text{CO}_3^{(\text{s})} + 4\text{H}^+(\text{aq}) \rightarrow 2\text{Cu}^{2+}(\text{aq}) + \text{CO}_2(\text{g}) + 3\text{H}_2\text{O}^{(l)}
\]

Combining equations (1) and (2), an equation that describes the dissolution process of malachite in MSA solutions was obtained:

\[
\text{Cu}_2(\text{OH})_2\text{CO}_3^{(s)} + 4\text{CH}_3\text{SO}_3\text{H}^{(\text{aq})} \rightarrow 2\text{Cu}^{2+}(\text{aq}) + 4\text{CH}_3\text{SO}_3^{3(\text{aq})} + \text{CO}_2(\text{g}) + 3\text{H}_2\text{O}^{(l)}
\]
3. Results and Discussion

3.1 Effect of MSA concentration

The effect of MSA concentration on the dissolution efficiency of copper as a function of time is shown in Figure 2a. Here, samples of 0.137 mm average particle size at a reaction temperature of 318 K and a stirring speed of 500 rpm were used. The copper leaching fraction increased with increasing leaching time and initial MSA concentration. Copper extraction increased from 61.39% to 84.07% after 60 min when the concentration of MSA was increased from 0.18 mol/L to 0.36 mol/L. No significant difference was observed in the results obtained within the MSA concentration range of 0.36 mol/L to 0.54 mol/L. Therefore, 0.36 mol/L of MSA was selected for further investigations, which revealed another advantage of MSA for extracting copper from malachite, namely that higher concentrations are required when other leaching reagents are used to leach malachite.

3.2 Effect of temperature

Several experiments, each lasting 60 min, were carried out to investigate the effect of reaction temperature on the dissolution of malachite with an average particle size of 0.137 mm at an initial MSA concentration of 0.36 mol/L and a stirring speed of 500 rpm. The results in Figure 2b indicate that temperature had a profound effect on the copper leaching fraction, and the copper leaching fraction increased with increasing temperature because of the active molecular motion. When the temperature was increased from 298 K to 338 K, copper extraction increased from 53.22% to 77.85% after 30 min. The copper leaching fraction reached 92.41% at 338 K after 60 min. It is known that higher temperature will lead to higher cost and operation requirement. Compared with the increase in reaction temperature from 298 K to 318 K, there is no significant effect on malachite leaching when the temperature is further elevated. Allowing for the leaching efficiency of copper, cost and operation requirement, the optimal reaction temperature was determined as 318 K.

3.3 Effect of particle size

The relationship between copper extraction and the average particle size is shown in Figure 2c. During the dissolution process, the initial MSA concentration, reaction temperature, and stirring speed were maintained constant at 0.36 mol/L, 318 K, and 500 rpm, respectively. As shown in Figure 2c, the dissolution rate increased as the particle size decreased, which is possibly attributed to the increase in active sites on the mineral surface when the particle size is decreased. This increase is beneficial for malachite to react with the reactant. However, particle size presents a relatively modest effect on leaching rate at appropriate leaching reagent concentration and reaction temperature, so no significant difference was observed in the range of the average particle sizes.

3.4 Effect of stirring speed

The effect of stirring speed on malachite dissolution was investigated in a stirring speed range of 300 rpm to 700 rpm at an initial MSA concentration of 0.36 mol/L, reaction temperature of 318 K, and particle size of 0.137 mm. Figure 2d shows that the increase in stirring speed from 300 to 600 rpm improved the copper leaching fraction, but a further increase in the stirring speed to 700 rpm did not cause any further increase in the dissolution efficiency of malachite. At low stirring speed, the mineral particles can not be dispersed in the solutions and remain at the bottom of the reactor. However, in this case, the solid particles were ground, resulting in an improvement in the leaching fraction of copper. When an adequate suspension
of the mineral particles was reached, the mechano-chemical effect became less important, but this effect can bring mineral particles into adequate contact with leaching reagents to enhance the dissolution efficiency of malachite. Thus, no significant difference was observed in the stirring speed range.

Figure 2. Effect of operation parameters on the leaching efficiency of copper: (a) MSA concentration, (b) temperature, (c) particle size, and (d) stirring speed.

3.5 Kinetic study

A kinetic study of a leaching reaction is essential for determining the optimum operation parameters for the application of the leaching process in a hydrometallurgical plant, because the study benefits the practical operation conditions and the productivity of metal extraction. The leaching process of malachite in MSA solutions is a heterogeneous reaction. In this reaction system, most reactions follow a shrinking core model (SCM), which can approximately express the dissolution performance of particles. According to this model, the rate of the controlling step of the dissolution process is divided into three independent models [2]. The following expressions can be used to describe the dissolution kinetics of the process:

For liquid film diffusion control:  
\[ x = k_l t \]  
(4)

For surface chemical reaction control:  
\[ 1 - (1 - x)^{1/3} = k_r t \]  
(5)

For film diffusion control through the product layer:  
\[ 1 - 3(1 - x)^{2/3} + 2(1 - x) = k_d t \]  
(6)

where \( x \) is the conversion fraction of solid particles, \( k_i, k_r, \) and \( k_d \) are the apparent rate constants for different
control steps, respectively, and \( t \) is the reaction time.

Based on equations (4), (5), and (6), in which the rate-controlling step is represented by liquid film diffusion control, the plot of \( x \) versus the reaction time is a straight line with a slope of \( k_f \). Similarly, the plot of \( 1 - (1 - x)^{1/3} \) and \( 1 - 3(1 - x)^{2/3} + 2(1 - x) \) versus the reaction time is also a straight line with a slope of \( k_r \) and \( k_d \) for surface chemical reaction control and film diffusion control through the product layer, respectively.

For the kinetic analysis in the present work, the SCMs with liquid film diffusion, surface chemical reaction, and film diffusion through the product layer as the rate-controlling steps, equations (4), (5), and (6), were evaluated. Kinetic data obtained from these three models were assessed using the correlation coefficient \( R^2 \) values in Table 2. The data in Table 2 show that the \( R^2 \) values for the liquid film diffusion control model and the chemical reaction control model are below 0.50 and 0.76, respectively, which implies a poor fit. As shown in Table 2, higher regression coefficient values were obtained for the film diffusion control through the product layer model. However, the dissolution rates obtained were fairly sensitive to temperature as shown in Figure 2b and the activation energy calculated based on the Arrhenius equation was 20.34 kJ/mol. These findings indicate that the film diffusion control through product layer model failed to represent the rate-controlling step. Thus, other kinetic models were utilized to describe the dissolution reaction. Among the various other kinetic models published in the literature, we found the following model proposed by Dickinson and Heal [27] to be suitable to describe the dissolution of malachite in MSA solutions.

\[
(1/3)\ln(1-x) + (1-x)^{-1/3} - 1 = k_{at}t
\]  

(7)

<table>
<thead>
<tr>
<th>Table 2. Correlation coefficient values ( R^2 ) of three kinetic models for various experimental data.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental variables</strong></td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>MSA concentration (mol/L)</td>
</tr>
<tr>
<td>0.18</td>
</tr>
<tr>
<td>0.27</td>
</tr>
<tr>
<td>0.36</td>
</tr>
<tr>
<td>0.45</td>
</tr>
<tr>
<td>0.54</td>
</tr>
<tr>
<td>Temperature (K)</td>
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<tr>
<td>298</td>
</tr>
<tr>
<td>308</td>
</tr>
<tr>
<td>318</td>
</tr>
<tr>
<td>328</td>
</tr>
<tr>
<td>338</td>
</tr>
<tr>
<td>Particle size (mm)</td>
</tr>
</tbody>
</table>

- 164 -
Plots of \((1/3)\ln(1-x) + (1-x)^{1/3} - 1\) versus time as a function of MSA concentration, temperature, particle size, and stirring speed are shown in Figure 3. The kinetic analysis results, including apparent rate constants and corresponding correlation coefficient values, are presented in Table 3. The results shown in Figure 3 and Table 3 illustrate that the dissolution of malachite follows the kinetic model presented in equation (7).

![Figure 3](image-url)
The kinetic equation for copper extraction from malachite can be expressed as:

\[
\frac{1}{3}\ln(1 - x) + (1 - x)^{-1/3} - 1 = k_0 \cdot (C)^{\alpha} \cdot (PS)^{\beta} \cdot (SS)^{\gamma} \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot t
\]  

where \(C\), \(PS\), \(SS\), \(E_a\), \(R\), and \(T\) represent the MSA concentration, particle size, stirring speed, activation energy, universal gas constant, and temperature, respectively. The constants \(\alpha\), \(\beta\), and \(\gamma\) are the reaction orders for the related parameters, and \(k_0\) is the frequency or pre-exponential factor.

The values of \(\alpha\), \(\beta\) and \(\gamma\) were determined to be 1.4452, \(-0.3452\), and 0.5985, respectively, according to Figure 4. The activation energy may be calculated based on the Arrhenius equation, and the Arrhenius plot of the dissolution process is shown in Figure 4b. According to the data from Figure 4b, the activation energy was determined to be 24.48 kJ/mol. Substituting the values of \(\alpha\), \(\beta\), \(\gamma\) and \(E_a\) into equation (8), the value of \(k_0\) was calculated to be approximately 1.84. Thus, the equation representing the dissolution kinetics of malachite in MSA solutions can be expressed as follows:

\[
\frac{1}{3}\ln(1 - x) + (1 - x)^{-1/3} - 1 = 1.84 \cdot (C)^{1.4452} \cdot (PS)^{-0.3452} \cdot (SS)^{0.5985} \cdot \exp\left(-24.48/RT\right) \cdot t
\]  

Figure 4. Plot of \(\ln k\) versus operation parameters: (a) MSA concentration, (b) temperature, (c) particle size, and (d) stirring speed.
Table 3. The apparent rate constants $k_m$ for $(1/3)\ln(1-x) + (1-x)^{-1/3} - 1$ and its corresponding correlation coefficient values $R^2$ for various experimental data.

<table>
<thead>
<tr>
<th>Experimental variables</th>
<th>$(1/3)\ln(1-x) + (1-x)^{-1/3} - 1$</th>
<th>$k_m$ (min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSA concentration (mol/L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.18</td>
<td></td>
<td>0.0012</td>
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<tr>
<td>0.27</td>
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<td>0.0022</td>
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<td>0.36</td>
<td></td>
<td>0.0034</td>
<td>0.9989</td>
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<tr>
<td>0.45</td>
<td></td>
<td>0.0045</td>
<td>0.9993</td>
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<tr>
<td>0.54</td>
<td></td>
<td>0.0059</td>
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<td>Temperature (K)</td>
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<td>298</td>
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<td>Particle size (mm)</td>
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<td>0.137</td>
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<td>0.0034</td>
<td>0.9989</td>
</tr>
<tr>
<td>0.075</td>
<td></td>
<td>0.0042</td>
<td>0.9985</td>
</tr>
<tr>
<td>0.053</td>
<td></td>
<td>0.0048</td>
<td>0.9983</td>
</tr>
<tr>
<td>Stirring speed (rpm)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>300</td>
<td></td>
<td>0.0026</td>
<td>0.9989</td>
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<tr>
<td>400</td>
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<td>0.0030</td>
<td>0.9997</td>
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<td>500</td>
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<tr>
<td>700</td>
<td></td>
<td>0.0043</td>
<td>0.9989</td>
</tr>
</tbody>
</table>

4. Conclusion

The dissolution kinetics of copper from malachite in MSA solutions was investigated. It was found that the main parameters in the experiments were determined to be leaching time, leaching reagent concentration, reaction temperature, particle size and stirring speed. The dissolution rate was determined to increase with increasing MSA concentration, reaction temperature, stirring speed, and decreasing particle size. A new shrinking core model, which is based on the interfacial transfer and diffusion through the product layer, was found to be a suitable representation of the rate-controlling step for copper from malachite in MSA solutions. The apparent activation energy of the dissolution reaction was 24.48 kJ/mol. The dissolution kinetics of malachite in MSA solutions can be expressed as equation (9).
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References