Original Article

Dissolution kinetics of hemimorphite in trichloroacetic acid solutions

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A B S T R A C T

In this study, the dissolution kinetics of hemimorphite in the presence of the organic reagent, trichloroacetic acid (TCAA), was investigated. Experimental variables such as reaction temperature (293–323 K), TCAA concentration (0.084–0.184 mol/dm 3), particle size (0.081–0.214 mm), and stirring speed (200–650 rpm) were studied to determine the influence on the zinc dissolution rate, and a kinetic model was developed to represent the relationship. The results demonstrated that during the leaching process, zinc was rapidly dissolved in TCAA and the zinc leaching rate increased as a function of increased reaction temperature, TCAA concentration, and stirring speed, and decreased particle size. Among the kinetic models of the porous solids tested, a new variant of the shrinking-core model well described the zinc leaching kinetics. The activation energy was determined to be 54.94 kJ/mol, and the rate of reaction equation \[1 - (2/3)x - (1 - x)^{2/3} = [11.24(\text{exp}(18.0994PS)^{-2.0837(\text{exp}((-54.94/RT))]), \text{also obtained to describe the process.}

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1. Introduction

Zinc is an important nonferrous metal that is highly ductile and resistant to corrosion and wear, and as such, is widely used in the manufacturing of alloys, rubbers, die castings, and is used as a galvanizing metal. Additionally, zinc is also employed within medical and chemical engineering applications [1–5]. Similar to copper and lead, natural zinc enrichment principally derives from zinc sulfide ores, which are easy to separate from gangue minerals by flotation techniques [6–8]. Zinc sulfide ores are rapidly depleting with increased zinc consumption. Therefore, steps to improve the efficiency and use of zinc oxide ores such as zincite, smithsonite, hydrozincite, willemite, hemimorphite and zinc
silicate is an increasingly significant area of research development [9–13].

Extensive investigations on the treatment of zinc silicate ores by using hydrometallurgical and pyrometallurgical methods have been reported [14]. Over the past few decades, pyrometallurgical research has been conducted on the treatment of low-grade ores. However, pyrometallurgical methods are not commercially practiced because of the resulting heavy pollution, high capital investment and high energy consumption. In recent years, research has focused on hydrometallurgical methods used to leach zinc from zinc oxide ores in the presence of various leaching agents, such as acids, caustic soda, sodium hydroxide, and ammoniacal solutions [15–18]. Among the leaching agents, sulfuric acid is the most common and is generally used to leach high-grade zinc oxide ores. Conversely, for low-grade zinc ores—especially those containing high Fe-bearing, calcium, carbonates and magnesium chloride—using sulfuric acid to leach zinc consumes a significant volume of acid, and results in a poor leaching result and a complex purification process [12,19,20]. Zhang et al. used sulfuric acid to leach zinc from a low-grade zinc oxide ore comprising high levels of silicon, and the results indicated that under optimal conditions, zinc leaching was 99.22% and the dissolution of silica was as low as 0.56% [21]. Xu et al. used sulfuric acid to leach zinc from a sulfide complex and a silicate-containing zinc ore, and 97% of zinc was leached after a reaction time of 150 min at 413 K, demonstrating that the complex zinc ore can be easily dissolved in sulfuric acid [22].

Hemimorphite comprises a three-dimensional framework composed of three-membered rings of one SiO$_4$ tetrahedron and two ZnO$_2$(OH)$_2$ tetrahedrons oriented perpendicular to the (011) plane—the reason why zinc is difficult to leach from hemimorphite. Zn can be ejected from the framework only by breaking the SiO$_4$ and ZnO$_2$(OH)$_2$ three-membered rings, thus, the technology has focused on zinc recovery by leaching silica [2,23]. Furthermore, there are reports demonstrating the influence of a series of zinc acid-leaching reactions from hemimorphite ores [24–26]. Xu et al. used a dilute sulfuric acid solution to leach zinc from hemimorphite and reported the dissolution kinetics and a mathematical model. Their research demonstrated that specific experimental parameters including time, temperature, sulfuric acid concentration and particle size influences zinc extraction. Additionally, the activation energy in the leaching process was calculated to be 44.90 kJ/mol and the rate-controlling step was determined to be the diffusion, as modeled by the shrinking core model. Rao et al. used iminodiacetic acid to leach zinc from hemimorphite and observed that hemimorphite is easily dissolved in iminodiacetic acid, and a zinc extraction of 88.15% was reported. Furthermore, as the isoelectric point of iminodiacetic acid was recovered by the addition of dilute sulfuric acid, this method is an environmental friendly process.

Conversely, alkaline solutions such as, ammonium chloride/sulfate and the addition of CaO, CaF$_2$ and NaF to leach zinc from hemimorphite, have also been reported [2,27,28,17]. The dissolution kinetics of hemimorphite in a solution of ammonium chloride was investigated. The results demonstrated that under optimal conditions, the leaching process can be controlled by the Elovich equation, and the activation energies of 405.14 kJ/mol and 239.61 kJ/mol for leaching temperatures of 348–363 K and 363–381 K, respectively, were reported [27]. Li et al. [2] studied the solubility of hemimorphite in an ammonium sulfate solution at 393 K. The results showed that the dissolution of zinc and silica from hemimorphite in an ammonium sulfate solution is selective and efficient. The solubility of zinc and silica in solution increases as a function of increased ammonium sulfate concentration. Yuan et al. [17] used an alkaline-based dissolution method to leach zinc from hemimorphite, and the results demonstrated that the recovery of zinc derived from hemimorphite was improved with increased reaction time. Xiong et al. [28] investigated Zn reduction by the vacuum carbothermic reduction of hemimorphite, with or without the addition of a CaF$_2$ catalyst. The experimental results indicated that zinc silicate can be catalyzed by CaF$_2$ resulting in a decrease of reaction temperature and time. Reaction temperature can be further decreased by increasing the CaF$_2$ catalyst loading. To obtain a zinc reduction rate of 93% from hemimorphite, the following operational parameters were employed: 10% CaF$_2$, 1373 K, 20 kPa, 40 min and a molar ratio of C to Zn (total) of 2.5.

The present study aims to provide an alternative method to leach zinc from hemimorphite and to investigate the effect of experimental parameters. TCAA is a member of the family of compounds known as chloroacetic acids, which includes mono-, di- and trichloroacetic acid [29]. TCAA is mainly used for organic synthesis, pharmaceuticals, chemical reagents and insecticides. Herein, the influence of TCAA on the leaching of zinc from hemimorphite is investigated together with the dissolution kinetics of the leaching process. The effects of reaction temperature, leaching agent concentration, particle size, and stirring speed on the hemimorphite dissolution ratio are also studied.

### 2. Experimental

#### 2.1. Materials and methods

Hemimorphite samples were collected from Yunnan Province, China, following the manual removal of gangue minerals, such as cerussite and calcite. The hemimorphite samples were hand-crushed, ground with three-head grinders, and finally sieved using standard test sieves to obtain the required particle size for dissolution experiments. Chemical analyses of the sample showed that hemimorphite contains 52.96% Zn, which indicated the high purity of the hemimorphite samples. The chemical compositions of the materials are shown in Table 1. X-ray diffraction (XRD) was performed using a Rigaku D/max 2500VB+18 kW powder diffractometer equipped with a Cu/K$_\alpha$ X-ray source, operating at 40 kV and 40 mA. XRD analyses of the materials are shown in Fig. 1, and demonstrate the presence of phase-pure hemimorphite. Analytical grade TCAA was used in this study. Pure deionized water was used for all

### Table 1 - Chemical composition of materials.

<table>
<thead>
<tr>
<th>Component</th>
<th>Zn</th>
<th>Fe</th>
<th>Pb</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content%</td>
<td>52.96</td>
<td>0.11</td>
<td>0.01</td>
<td>24.42</td>
<td>0.077</td>
<td>0.033</td>
<td>0.103</td>
</tr>
</tbody>
</table>
2.2. Dissolution experiments

The leaching process was performed in a 500 cm³ wide-mouth beaker batch reactor having a digitally controlled mechanical stirrer, a condenser to prevent evaporation loss, a thermometer to control temperature, and a thermostatically controlled water bath for heating. In a typical experiment, 5 g of hemimorphite, having the required particle size, was added to 500 cm³ of freshly prepared TCAA solutions of varying concentration. Thereafter, the temperature was adjusted to the desired set point and the suspension stirred at the desired stirring speed. All experiments maintained the solid concentration of 1:100 g/cm³. After the required reaction time, a 5 cm³ sample aliquot was accurately withdrawn periodically to analyze Zn concentration by AAS.

3. Results and discussion

3.1. Dissolution reaction

TCAA (-COOH) is a strong organic acid that can be easily deprotonated, hence hydrogen can transfer to metal complexes, e.g. zinc or other metals. TCAA in aqueous medium follows the reaction:

\[ \text{Cl}_3\text{COCOOH} \rightarrow \text{Cl}_3\text{COCOO}^{\text{aq}}^- + \text{H}^{\text{aq}}^+ \]  

or

\[ \text{Cl}_3\text{COCOO}^- + \text{H}_2\text{O}^{\text{aq}} \rightarrow \text{Cl}_3\text{COCOO}^{\text{aq}}^- + \text{H}_3\text{O}^{\text{aq}}^+ \]  

When hemimorphite [\(\text{Zn}_4\text{Si}_2\text{O}_7\text{(OH)}_2\cdot\text{H}_2\text{O}\)] is added to a TCAA solution, the reaction during dissolution is expected to be as follows:

\[ \text{Zn}_4\text{Si}_2\text{O}_7\text{(OH)}_2\cdot\text{H}_2\text{O} + 8\text{H}^{\text{aq}}_2 \rightarrow 4\text{Zn}^{2+} + 2\text{SiO}_2^{\text{aq}} + 6\text{H}_2\text{O}^{\text{aq}}_2 \]  

Consequently, the overall leaching reaction can be expressed as follows:

\[ \text{Zn}_4\text{Si}_2\text{O}_7\text{(OH)}_2\cdot\text{H}_2\text{O}^{\text{aq}} + 8\text{Cl}_3\text{COCOO}^{\text{aq}}^- \rightarrow 4\text{Zn}^{\text{aq}}_2\text{COCOO}^{\text{aq}}^- + 2\text{SiO}_2^{\text{aq}} + 6\text{H}_2\text{O}^{\text{aq}}_2 \]  

(4)

3.2. Effect of temperature

Reaction temperature is an increasingly important factor for zinc extraction. All other operational parameters were kept constant as follows: the solid concentration of 1:100 g/cm³, a particle size of 0.151 mm, an initial TCAA concentration of 0.150 mol/dm³, and a stirring speed set to 500 rpm. The effect of reaction temperature was investigated at 10 K increments across the temperature range of 293–323 K. The leaching results are shown in Fig. 2(a). Zinc leaching fractions increased as a function of reaction temperature. At 293 K, only 67.79% of Zn was leached in a dissolution time of 5 min, whereas, zinc leaching fractions increased to 94.35% when increasing the temperature to 293 K, for the same dissolution time.

3.3. Effect of TCAA concentration

The effect of TCAA concentration on the zinc leaching rate was investigated under fixed experimental conditions: leaching temperature of 313 K, the solid concentration of 1:100 g/cm³, hemimorphite particle size of 0.151 mm, a stirring speed of 500 rpm and a leaching time of 5 min. The results are presented in Fig. 2(b). As observed in Fig. 2(b), the zinc leaching fraction increases significantly as a function of initial TCAA concentration. At an initial TCAA concentration of 0.184 mol/dm³, the zinc leaching rate was observed to be 97.15%, and hemimorphite was almost completely dissolved. Conversely, decreasing the initial TCAA concentration to 0.084 mol/dm³ resulted in a Zn leaching rate of only 60.67% when subjected to the same conditions. At lower initial TCAA concentrations, it is observed that TCAA preferentially dissolves quartz, calcium, and other alkaline gangue minerals. However, it is also observed that the zinc leaching rate increases as a function of increased initial TCAA concentration. At relatively high concentrations of TCAA, the H⁺ concentration gradients vary between internal and external ores, therefore, the initial TCAA concentration has the biggest influence on hemimorphite dissolution.

3.4. Effect of particle size

The effect of particle size on the zinc leaching rate was evaluated under the solid concentration of 1:100 g/cm³, a leaching temperature of 313 K, an initial TCAA concentration of 0.150 mol/dm³, and a stirring speed of 500 rpm. Hemimorphite samples of four experimental average particle sizes (0.081 mm, 0.106 mm, 0.151 mm and 0.214 mm) were used in the dissolution experiments. The results are displayed in Fig. 2(c). Zinc leaching fractions increased as the particle size decreased (Fig. 2(c)). After a reaction time of 5 min, the zinc leaching fractions was measured at only 66.87% for a 0.214 mm
3.5. Effect of stirring speed

Zinc leaching fractions were studied as a function of stirring speed at 200, 350, 500, and 750 rpm. Hemimorphite samples having an average particle size of 0.151 mm were subjected to an initial TCAA concentration of 0.15 mol/dm$^3$ and a reaction temperature of 313 K for 5 min. The results are shown in Fig. 2(d). The zinc leaching rate enhanced with the increased stirring speed from 68.75% to 93.41% as a result of increasing the stirring speed from 200 rpm to 650 rpm, which indicated that the dissolution rate was influenced by the stirring speed. However, at low stirring speeds, the hemimorphite particles could not be maintained in a state of dispersion and remained at the bottom of the reactor. In this case, the results of the zinc dissolution efficiency are not reliable.

4. Kinetics study

As the need for a cost-effective zinc extraction process is becoming more important, developments to enhance the productivity of zinc extraction, by adopting changes to the process conditions, is essential. However, no information on the dissolution kinetics of hemimorphite in TCAA has been reported, hitherto. Therefore, reporting the dissolution kinetics of zinc leaching from hemimorphite in TCAA is an important development that will contribute to improving the productivity of zinc extraction.

Using TCAA to leach zinc from hemimorphite is a complicated reaction process. The leaching reaction of mineral particles by a solid-fluid reaction is represented by the following reaction:

$$\text{aAfluid} + \text{bBsolid} \rightarrow \text{product}$$  \hspace{1cm} (5)

where $a$ and $b$ are the stoichiometric coefficients, and $A$ and $B$ represent the fluid reactant and solid undergoing dissolution, respectively. Dissolution reaction kinetics is often described by the shrinking core model. According to this model, the leaching process is controlled by either diffusion through the liquid film, a surface chemical reaction, or diffusion through the product layer [31–33].

If the leaching rate is controlled by diffusion through the liquid film, the integrated rate equation of the shrinking core model can be described as follows:

$$k_1 t = x$$  \hspace{1cm} (6)
Table 2 – The correlation coefficient values ($R^2$) of three kinetic models as a function of experimental variables.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Diffusion through the liquid film $x$</th>
<th>Surface chemical reaction $1-(1-x)^{1/3}$</th>
<th>Diffusion through the product layer $1-(2/3)x-(1-x)^{2/3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$R^2$</td>
<td>$k_4$ (min$^{-1}$)</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>0.17432</td>
<td>0.68263</td>
<td>0.07821</td>
</tr>
<tr>
<td>303</td>
<td>0.20866</td>
<td>0.70039</td>
<td>0.1046</td>
</tr>
<tr>
<td>313</td>
<td>0.23289</td>
<td>0.66402</td>
<td>0.1286</td>
</tr>
<tr>
<td>323</td>
<td>0.24835</td>
<td>0.62789</td>
<td>0.14949</td>
</tr>
<tr>
<td>TCAA concentration (mol/dm$^3$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.084</td>
<td>0.15245</td>
<td>0.6864</td>
<td>0.06573</td>
</tr>
<tr>
<td>0.117</td>
<td>0.20022</td>
<td>0.6578</td>
<td>0.09844</td>
</tr>
<tr>
<td>0.150</td>
<td>0.23016</td>
<td>0.63052</td>
<td>0.12834</td>
</tr>
<tr>
<td>0.184</td>
<td>0.25413</td>
<td>0.58091</td>
<td>0.16655</td>
</tr>
<tr>
<td>Particle size (mm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.214</td>
<td>0.17121</td>
<td>0.70416</td>
<td>0.07636</td>
</tr>
<tr>
<td>0.151</td>
<td>0.20252</td>
<td>0.65913</td>
<td>0.09812</td>
</tr>
<tr>
<td>0.106</td>
<td>0.22952</td>
<td>0.63241</td>
<td>0.12353</td>
</tr>
<tr>
<td>0.081</td>
<td>0.24525</td>
<td>0.59672</td>
<td>0.14368</td>
</tr>
<tr>
<td>Stirring speed (rpm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.17611</td>
<td>0.70012</td>
<td>0.07966</td>
</tr>
<tr>
<td>350</td>
<td>0.20363</td>
<td>0.67632</td>
<td>0.09999</td>
</tr>
<tr>
<td>500</td>
<td>0.22682</td>
<td>0.63341</td>
<td>0.12151</td>
</tr>
<tr>
<td>650</td>
<td>0.24578</td>
<td>0.60095</td>
<td>0.14518</td>
</tr>
</tbody>
</table>

If the reaction rate is controlled by a surface chemical reaction, the integrated rate equation of the shrinking core model can be described as follows:

$$k_t t = 1 - (1 - x)^{1/3}$$  \hspace{1cm} (7)

If the reaction rate is controlled by diffusion through the product layer, the integrated rate equation of the shrinking core model can be described as follows:

$$k_d t = 1 -(2/3)x - (1-x)^{2/3}$$  \hspace{1cm} (8)

where $x$ is the solid particle conversion fraction, $k_1$ is the apparent rate constant for the diffusion through the fluid film, $k_t$ is the apparent rate constant for the surface chemical reaction, $k_d$ is the apparent rate constant for the diffusion through the product layer, and $t$ is the reaction time.

When hemimorphite is dissolved in TCAA solutions, the mineral particles and leaching agent will react, forming soluble zinc trichloroacetic. Insoluble products were not formed during the leaching of hemimorphite. In the aforementioned models, when the rate-controlling step is represented by diffusion through the fluid film, the plot of $x$ versus reaction time should be a straight line with a slope of $k_1$; when the rate-controlling step is represented by a surface chemical reaction, the plot of $1 -(1 - x)^{1/3}$ versus reaction time should be a straight line with a slope of $k_t$. Regarding kinetic analysis, the shrinking core model—modeling for diffusion through the fluid film and surface chemical reactions as the rate-controlling steps—$k_1=x$, $k_t=1 -(1 - x)^{1/3}$ and $k_d = 1 -(2/3)x - (1-x)^{2/3}$ were evaluated. The experimental data obtained from the leaching step were analyzed based on the shrinking core model using the rate expression given in Eqs. (6)–(8) to determine the dissolution kinetic parameters and the rate-controlling step of hemimorphite leaching in TCAA. Data were assessed using the correlation coefficient, $R^2$, values in Table 2. $R^2$ values for $1 -(2/3)x - (1-x)^{2/3}$ are below 0.93, which implies a poor fit. Therefore, diffusion through the fluid film and surface chemical reaction models do not adequately represent the rate-controlling step. Thus, other kinetic models were used to describe the dissolution reaction.

On the basis of the various kinetic models published in the literature, we observed that the dissolution of hemimorphite in TCAA solutions can be described using the following model:

$$k_m t = [1 -(2/3)x - (1-x)^{2/3}]^2$$  \hspace{1cm} (9)

where $k_m$ is the apparent rate constant for the surface chemical reaction model. Plots of $[1 -(2/3)x - (1-x)^{2/3}]^2$ versus time, as a function of temperature, TCAA concentration, particle size, and stirring speed are shown in Fig. 3. The apparent rate constants for $[1 -(2/3)x - (1-x)^{2/3}]^2$ and the corresponding $R^2$ values, as a function of various experimental variables, are shown in Table 3. The results from Fig. 3 and Table 3 demonstrate that the leaching kinetics of hemimorphite dissolution followed the model presented in Eq. (9). Combined with the experimentally-obtained data analysis, we concluded that this model is an intermediate model, and the rate is determined by the both the diffusion of the reagent to the particle surface at the solution-particle interface, and the rate of the surface dissolution reaction. The rate of this process is proportional to the reagent concentration in the solution, and the reagent concentration reflects the reaction order with regard to the reagent.
The kinetic equation, corresponding to zinc extraction from hemimorphite, can be expressed as follows:

\[
[1 - (2/3)x - (1 - x)^{2/3}]^2 = k_0(C)^\alpha(PS)^\beta(SS)^\gamma \exp \left( -\frac{E_a}{RT} \right) t \tag{10}
\]

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

The values of \( \alpha, \beta, \gamma \) and \( E_a \) are 3.80946, −2.00833, and 1.62147, respectively. According to the results shown in Fig. 4, \( E_a \) can be calculated by the Arrhenius equation. Additionally, the Arrhenius plot of the dissolution process (Fig. 4(a)) shows that the activation energy is 54.94 kJ/mol. By substituting in the values of \( \alpha, \beta, \gamma \), and \( E_a \) into Eq. (10), the value of \( k_0 \) was calculated to be approximately 11.24. Thus, the equation representing the hemimorphite dissolution kinetics in the TCAA solution can be expressed as follows:

\[
[1 - (2/3)x - (1 - x)^{2/3}]^2 = 11.24(C)^{3.80946}(PS)^{-2.00833}(SS)^{1.62147} \exp \left( -\frac{54.94}{RT} \right) t \tag{11}
\]
5. Conclusions

The dissolution kinetics of hemimorphite in TCAA solutions was investigated. TCAA was observed to be a feasible and economic leaching agent to leach hemimorphite, as the mineral was easily dissolved in the presence of TCAA and a high zinc leaching fraction was obtained after a reaction time of only 5 min. The dissolution rate of hemimorphite increased as a function of increased reaction temperature, leaching reagent concentration, and stirring speed, and decreased particle size. We also observed that the leaching reagent concentration exerted a significant influence on the zinc leaching rate. A reaction temperature of 313 K only resulted in a mild leaching environment. Hemimorphite having an average particle size of 0.151 mm afforded appropriate active sites on the mineral surface, while stirring the suspension at 500 rpm was sufficient to fully suspend the mineral particles. The dissolution process followed the kinetic law of the shrinking core model, and a new kinetic model \( (1 - (2/3)x - (1 - x)^{2/3})^2 = 11.24(C)^{3.80948}(PS)^{-2.00833}(SS)^{1.62147}\exp(-54.94/RT) \) was found to be suitable to represent the rate-controlling step, with an apparent activation energy value of 54.94 kJ/mol.

Conflicts of interest

The authors declare no conflicts of interest.

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