Original Article

Alkaline leaching of lead and zinc by sodium hydroxide: kinetics modeling

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ABSTRACT

This study was performed in two phases of work. In the first stage, alkaline leaching of lead and zinc from an Iranian low-grade oxide ore was examined and the influence of the operating variables including stirring speed, leaching temperature, NaOH concentration and liquid to solid ratio was determined experimentally. The optimum condition was found to be NaOH concentration of 4 M, liquid to solid ratio of 20 ml/g, temperature of 80 °C and a stirring speed of 500 rpm for lead and 400 rpm for zinc, in the range of investigated parameters. Under these conditions, the highest recovery of lead and zinc was obtained to be 72.15 and 85.52%, respectively. In the second stage, the dissolution kinetics of lead and zinc was evaluated by the shrinking core models. The finding reveals that diffusion through the fluid film was the leaching kinetics rate controlling step of lead and zinc. The activation energy was found to be 13.6 kJ/mol for lead and 13.92 kJ/mol for zinc. Equations representing the leaching kinetics of lead and zinc were achieved to be \[ 1 - (1 - x)^{\frac{2}{3}} = 0.7272 \times e^{-13.6/8.314 \times 7} \times t \] and \[ 1 - (1 - x)^{\frac{2}{3}} = 0.9686 \times e^{-13.92/8.314 \times 7} \times t \], respectively.

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1. Introduction

The increasing demand for metals and metallic compounds in the world has required intensive studies for the extraction of metals from ores. Lead and zinc are important metals which are mostly extracted from sulfide ores. Lead and zinc resources have been continuously exploited and the high-grade ores have gradually become depleted, and low-grade oxide ores have been developed as important sources. Leaching process is the first step of hydrometallurgical methods which are used for extraction of metals [1]. Many research efforts were carried out to develop the hydrometallurgical method for increasing the recovery rate of lead and zinc. Inorganic acids have been commonly used as leach reagent in these studies [1–4]. In addition to this, organic acids have also been applied as leach reagents in recent years [5–8]. Additionally, much attention has been focused on the alkaline treatment of low-grade zinc oxide ores [9–14]. Meanwhile, there are many other reports that the different reagents have been used in the leaching of zinc-based research as discussed by Abkhoshk et al. [15]. Moreover, some research studies have also been conducted the treatment of lead ores by various leaching agents especially on the recovery and dissolution kinetics of
lead from oxidized resources and other lead-bearing renewable resources [16–20]. These efforts demonstrate that during the leaching process, sulfuric acid leaching is the most viable. Organic acids are attractive due to the ease of biodegradation and can be used at mildly acidic conditions (pH 3–5). Alkaline leaching acts generally more selective. In addition, it is considered to be cost-effective, simple and easy to be operated and managed to extract zinc from oxidized zinc ores or wastes, for the impurities such as Fe, Cu, Cd, Co, Ni, etc. it can hardly be leached out in alkaline media and its lower electricity consumption in electrowinning process compared with acidic electrowinning [9–11]. Hence, this study was focused on alkaline leaching of lead and zinc from a low-grade ore. In this study, the dissolution kinetics is examined according to the shrinking core models and the best kinetics model is chosen to describe the leaching process of lead and zinc.

2. Materials and methods

2.1. Materials

The required ore samples were obtained from the Iranshahr district (Goshfih mine tailings), which is located about 20 km southwest of the city of Isfahan in Iran. The samples were crushed and then ground to less than 150 µm. The phases of sample were characterized by XRD, which the main phases of lead and zinc identified from the XRD pattern included smithsonite (ZnCO₃) and cerussite (PbCO₃). The main chemical composition of samples was characterized by X-ray fluorescence. The results showed that the sample contained 5.91% ZnO and 5.32% PbO [21].

2.2. Experimental procedure

The dissolution process was carried out in a beaker of 500 ml, which heated a hot plate, equipped with a digital controlled magnetic stirrer and a thermometer for temperature control. A series of sodium hydroxide solution with concentration from 0.5 to 4 M were prepared as leaching agent and put into the beaker. According to the desired liquid to solid (L/S) ratio, 3 g of solid was added into the sodium hydroxide solution. Then solutions were mixed using a magnetic stirrer with a certain speed at the required temperature. When the dissolution process finished, the sample was filtered and the liquid phase was analyzed with AAS for the content of lead and zinc. The leaching rate of Pb and Zn was calculated according to the following formula:

$$ R = \frac{C_M \times V}{C_0 \times M} \times 100 $$

where R is the leaching recovery percentage of metal (Pb or Zn); C_M (g/L) is the concentration of metal ion (Pb or Zn) in the leach liquor; V (L) is the leach liquor volume; C_0 (%) is the metals content of Pb and Zn in oxide ore sample and M (g) is the mass of the Pb and Zn oxide ore.

3. Results and discussion

3.1. Effect of sodium hydroxide concentration

The alkaline concentration plays a very important role in the metals leaching process. To investigate the influence of NaOH concentration on the leaching rate of lead and zinc, the experiments were carried out in the leaching solutions containing different NaOH concentrations (0.5, 1, 2 and 4 M) at temperature of 70 °C, stirring speed of 500 rpm and L/S ratio of 20 ml/g, which the results are plotted in Fig. 1. When sodium hydroxide concentration increased from 0.5 M to 4.0 M, the percentage of leached Zn increased significantly from 24.12% to 80.92%, while the percentage of leached Pb increased from 23.55% to 64.01%. In fact, when the concentration of NaOH solution reaches 4 M, the hydroxyl ions are enough due to the further formation of Zn(OH)₂⁻ and Pb(OH)₂⁻ (Eqs. (2) and (3)) and therefore the leaching rate could be over 80.92% for zinc and 64.01% for lead.

$$ \text{PbCO}_3 + 4\text{OH}^- = \text{Pb(OH)}_4^{2-} + \text{CO}_3^{2-} $$

(2)

$$ \text{ZnCO}_3 + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} + \text{CO}_3^{2-} $$

(3)

3.2. Effect of liquid to solid (L/S) ratio

The phase ratio of liquid to solid is another important factor to influence the contact chance of hydroxyl ions with lead and zinc oxides. These experiments were carried out in 4 M NaOH solution for 90 min at 70 °C with stirring of 500 rpm. The experimental data for different L/S ratios ranging from 10 to 25 ml/g are illustrated in Fig. 2. As observed, the recovery of lead and zinc enhanced with increasing L/S ratio from 10 to 20 ml/g. However, further increase the L/S ratio to 25 ml/g, the leaching rate is reduced. Thus, L/S ratio of 20 is found to be optimal. According to Rao et al. [22], a higher L/S ratio is expected to reduce the viscosity of the slurry by facilitating better mixing, contributing to the reduction in diffusional mass transfer resistance. This phenomenon also can be understood from the mass transportation equilibrium between ZnO and PbO and the coordination ions Zn(OH)₂⁻ and Pb(OH)₂⁻ in the leaching solution.

3.3. Effect of stirring speed

The effect of stirring speed on the dissolution performance of lead and zinc samples was evaluated by regulating the stirring speed to 200, 300, 400 and 500 rpm at 70 °C, NaOH concentration of 4 M, and L/S ratio of 20 ml/g. Fig. 3 demonstrates that the stirring speed has an appreciable effect on the dissolution of lead and zinc. It can be seen that, after 90 min of dissolution, the leaching fraction of lead increases from 53.65 to 80.92% when the stirring speed increased from 200 to 500 rpm. It is also observed that, the stirring speed of 400 rpm is beneficial for the extraction of zinc to bring mineral particles into adequate contact with NaOH solution. According to Zhang et al.
[14], increasing the stirring speed promotes reactants diffusion from bulk solution to mineral surface and improves the leaching rate.

3.4. Effect of temperature

In order to investigate the effect of temperature on the dissolution of low-grade lead and zinc oxide ore, temperature was varied from 50 °C to 80 °C and experiments were performed at NaOH concentration of 4 M and L/S ratio of 20 ml/g with stirring speed of 500 rpm for lead and 400 rpm for zinc. The variation in the leaching ratio with various temperatures is shown in Fig. 4. It can be seen that, with increasing the temperature from 50 °C to 80 °C, the leached zinc increases from 49.28% to 72.15% after 90 min. It is also observed that the zinc leaching rate by NaOH is only 60.32% at 50 °C, but quickly enhances to 85.52% when the temperature is increased to 80 °C. According to Rao et al. [22], with enhancing the leaching temperature, the energy available for atomic and molecular collisions increases. In addition, mass transfer coefficient, reaction constant and diffusivity are all improved with the development of temperature. Thus, it can be found that a high enough temperature is necessary to activate the reagent and accelerate the reaction of hydroxyl ions with lead and zinc oxides in the alkaline leaching.

3.5. Kinetic modeling

Leaching kinetics plays an important role in the extraction of metals and compounds in an economical way. According to Wang et al. [23], it can be concluded that the leaching process in NaOH solution involves: (i) transport of NaOH from the bulk solution to the particle surface, (ii) diffusion of NaOH through the solid residual layer from the particle surface to the surface of the particle.
of unreacted core, (iii) reaction between NaOH and low-grade oxide ore on the surface of the unreacted core (Eqs. (2) and (3)), (iv) diffusion of the resultants through the solid residual layer from the reaction interface to the particle surface, and (v) transport of the resultants from the particle surface to the bulk solution. The reactions occurring during the leaching process are typically heterogeneous [24] and the relevant kinetics follows the shrinking core model which was described by Liddell in detail [25]. The following expressions can be used to describe the leaching process kinetics [3,26]:

For diffusion control through the fluid film:

\[ 1 - (1 - x)^{2/3} = k \times t \]  \hspace{1cm} (4)

For solid product diffusion control:

\[ 1 - 3(1 - x)^{2/3} + 2(1 - x) = k \times t \]  \hspace{1cm} (5)

For surface chemical reaction control:

\[ 1 - (1 - x)^{1/3} = k \times t \]  \hspace{1cm} (6)

where \( x \) is the fractional conversion of lead and zinc, \( t \) is the reaction time (min) and \( k \) is the apparent rate constant (min\(^{-1}\)). The overall rate of dissolution is controlled by the slowest of these sequential steps.

Values of Eqs. (4)–(6) versus the reaction time were plotted to determine the kinetic parameters and leaching rate controlling step, which the results are shown in Figs. 5 and 6. Leaching experiments were carried out at temperatures ranging from 50 to 80 °C in steps of 10 °C at NaOH concentration of 4 M and L/S ratio of 20 ml/g with a stirring speed of 400 rpm for zinc and 500 rpm for lead.

From the slopes of the straight lines the apparent rate constants, \( k \), were evaluated, which the rate constants calculated and their correlation coefficients are given in Figs. 5 and 6.

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**Fig. 3** – Effect of stirring speed on the leaching recovery of lead and zinc at temperature of 70 °C, NaOH concentration of 4 M and L/S ratio of 20 ml/g.

**Fig. 4** – Effect of temperature on the leaching recovery of lead and zinc at NaOH concentration of 4 M, stirring speed of 400 rpm for zinc and 500 rpm for lead and L/S ratio of 20 ml/g.
and Table 1. As seen, the highest $R^2$ values obtain for the fluid film diffusion and the surface chemical reaction. On the other hand, due to the small difference between surface chemical reaction control and liquid film diffusion control, it is difficult to distinguish between these two reaction models. Additionally, in leaching processes, dissolution ratio directly depends on the activation energy, which can be calculated based on the Arrhenius equation ($k = A \times e^{-E_a/R \times T}$). Based on the Arrhenius

<table>
<thead>
<tr>
<th>Metal</th>
<th>Temperature (°C)</th>
<th>Diffusion through the liquid film</th>
<th>Diffusion through the product layer</th>
<th>Surface chemical reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k$ (min$^{-1}$)</td>
<td>$R^2$</td>
<td>$k$ (min$^{-1}$)</td>
</tr>
<tr>
<td>Zinc</td>
<td>50</td>
<td>0.0047</td>
<td>0.9695</td>
<td>0.0014</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.0052</td>
<td>0.9847</td>
<td>0.0017</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.0061</td>
<td>0.9852</td>
<td>0.0025</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.0072</td>
<td>0.9786</td>
<td>0.0034</td>
</tr>
<tr>
<td>Lead</td>
<td>50</td>
<td>0.0055</td>
<td>0.9854</td>
<td>0.0022</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.0061</td>
<td>0.9853</td>
<td>0.0029</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.0077</td>
<td>0.9773</td>
<td>0.0046</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.0083</td>
<td>0.9711</td>
<td>0.0056</td>
</tr>
</tbody>
</table>
activation energy theory, Arrhenius equation was plotted as Ln (k) vs. (1/T) for each temperature and the activation energies were calculated from the slopes of straight lines where the slope is $-E_a/R$. The values of activation energies calculated from Arrhenius plot are shown in Table 2. For example, the Arrhenius plot of lead dissolution in NaOH solution based on the film diffusion model is shown in Fig. 7. It has been previously stated that the typical activation energy for a chemically controlled process is greater than 40 kJ/mol, while the activation energy of a diffusion controlled process is usually

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**Fig. 6** – Plot of the shrinking core models vs. leaching time at different temperatures for the dissolution reactions of zinc with NaOH solution.

**Table 2** – Values of activation energies calculated for leaching process of lead and zinc from low-grade oxide ores in sodium hydroxide solution.

<table>
<thead>
<tr>
<th>Kinetic equations</th>
<th>Metal</th>
<th>Activation energy ($E_a$, kJ/mol)</th>
<th>Arrhenius equation coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 - (1-x)^{2/3}$</td>
<td>Zn</td>
<td>13.92</td>
<td>$Y_{50} = 0.0055x + 0.044$ R$^2 = 0.9854$</td>
</tr>
<tr>
<td>$1 - 3(1-x)^{2/3} + 2(1-x)$</td>
<td>Pb</td>
<td>13.6</td>
<td>$Y_{50} = 0.0055x + 0.0075$ R$^2 = 0.9886$</td>
</tr>
<tr>
<td>$1 - (1-x)^{1/3}$</td>
<td></td>
<td>18.07</td>
<td>$Y_{50} = 0.0055x + 0.075$ R$^2 = 0.9886$</td>
</tr>
<tr>
<td>$1 - 3(1-x)^{2/3} + 2(1-x)$</td>
<td></td>
<td>13.6</td>
<td>$Y_{50} = 0.0055x + 0.0075$ R$^2 = 0.9886$</td>
</tr>
<tr>
<td>$1 - (1-x)^{1/3}$</td>
<td></td>
<td>18.07</td>
<td>$Y_{50} = 0.0055x + 0.0075$ R$^2 = 0.9886$</td>
</tr>
</tbody>
</table>

|                  |       | 221.54                           | Frequency factor (A, min$^{-1}$) |
|                  |       | 2.641                            |                                 |
|                  |       | 17.003                           |                                 |
|                  |       | 1.097                            |                                 |
below 40 kJ/mol \[24\]. According to Table 2, it can be concluded that leaching process of lead and zinc from low-grade oxide ore using sodium hydroxide is controlled by diffusion process. Consequently, the equations representing the kinetics of leaching process of lead and zinc can be expressed as according to Eqs. (7) and (8), respectively.

\[
1 - (1 - x)^{2/3} = 0.7272 \times e^{-13.6/8.314 \times T} \times t
\]

(7)

\[
1 - (1 - x)^{2/3} = 0.9686 \times e^{-13.92/8.314 \times T} \times t
\]

(8)

4. Conclusion

This study was carried out on alkaline leaching of an Iranian low-grade lead and zinc ore using sodium hydroxide solution. The results of this investigation can be summarized as follows:

(i) In the range of studied parameters, the most suitable conditions for the leaching process of lead and zinc attained at temperature 80 °C, 4 M NaOH, L/S ratio = 20 ml/g and an agitation speed of 500 rpm for lead leaching and 400 rpm for zinc dissolution. Under these conditions, it was found that a zinc leaching recovery of 85.5% with a lead leaching recovery of 72.15% could be obtained.

(ii) The dissolution kinetics of lead and zinc was examined according to the shrinking core models and it was distinguished that the leaching process of lead and zinc in sodium hydroxide solution followed the kinetic law of the shrinking core model with the fluid film diffusion as the rate-controlling step. The activation energies were determined to be 13.6 and 13.92 kJ/mol for the leaching of lead and zinc, respectively.

(iii) According to diffusion model through the fluid film and Arrhenius equation, equations representing the leaching process kinetics for lead and zinc were determined to be

\[
1 - (1 - x)^{2/3} = 0.7272 \times e^{-13.6/8.314 \times T}
\]

and

\[
1 - (1 - x)^{2/3} = 0.9686 \times e^{-13.92/8.314 \times T}, \text{ respectively.}
\]

Conflicts of interest

The authors declare no conflicts of interest.

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