Laboratory Simulation of In-situ Leaching of Polyhalite

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\begin{abstract}
Deeply buried polyhalite is a kind of sulfate which contains about 28\% potassium sulfate. Extraction potassium from polyhalite using in-situ leaching technology can help to resolve the problem of potassium shortage. This paper indicates a modeling study of leaching polyhalite in laboratory. Using CaCl\textsubscript{2} as lixiviant, the effect of the concentration of lixiviant, granularity of mineral, the infiltration velocity and the length of infiltration route are studied by analyzing potassium concentration in leaching solution. The experiment results show that the granularity of mineral is one of the most influencing factors to the recovery of K\textsuperscript{+}. When granularity of mineral is changed from 2-3mm to 5-8mm, the recovery of K\textsuperscript{+} decreased from 80.19\% to 42.17\%. The recovery of K\textsuperscript{+} increases with the infiltration velocity and the length of infiltration route and the concentration of K\textsuperscript{+} in lixiviating solution can be heightened to 12.1g/L by increasing the length of infiltration route. The lixiviation process matches the metal dissolution kinetic equation. According to the experiential results, the parameters in equation are calculated. When the infiltration velocity is increased from 0.159m/h to 0.318m/h, the leaching velocity changed from 0.278h\textsuperscript{-1} to 0.673h\textsuperscript{-1} and the time of metal fully leaching to solution changed from 2.333h to 0.951h.

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\textbf{Keywords:} polyhalite; potassium leaching; dissolution kinetics equation
\end{abstract}

\section{Introduction}

Polyhalite is widely distributed in China, such as in Sichuan[1]. It is difficult to use and mine for its complex ingredient, weak water-solubility and deeply buried (below 1000m)[2]. According to previous

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research [3-5], the solubility of polyhalite can be increased in some inorganic salt solution such as calcium chloride, barium chloride, ammonium carbonate, and by using CaCl₂ solution, the recovery of K⁺ from polyhalite could be higher than 85% and the equation concentration of polyhalite in CaCl₂ solution could also be 36g/L. By using in-situ leaching technology, the problem of deeply buried can be solved.

In this paper, using the CaCl₂ solution as the lixiviant to leach polyhalite, the influence of granularity of mineral, infiltration velocity and the length of infiltration route were mainly exterminated. Through it, the kinetic equation of in-situ leaching of polyhalite was obtained by using the water-soluble salt infiltration model based on the theory of dynamic diffusion in multiphase reactions founded by V.С.Гонюбен, Г.Н.Кривеци. And this kinetic equation maybe has a theoretical foundation for in-suit leaching technology of polyhalite.

2. Materials and methodology

2.1. Materials

The ore used in the experiment was picked from the Sichuan Qu Xian Nongle polyhalite mining area. The main chemical composition K⁺, Mg²⁺, Ca²⁺, SO₄²⁻ are 11.55, 6.76, 10.03 and 62.59 by mass respectively.

2.2. Methodology

2.2.1 Dissolution equation

In the process of in-situ leaching, the reaction equation of polyhalite and CaCl₂ can be expressed as following:

\[ K_2SO_4·MgSO_4·2CaSO_4·2H_2O + 2CaCl_2 = 2KCl + MgCl_2 + 4CaSO_4 + 2H_2O. \]

2.2.2 Infiltration experiment method

The leaching process was simulated by the column leaching experiment. The column installment structure is showed in figure 1. A plastic perforated plate was put on the infiltration column base, then loaded polyhalite which was well dispersed and covered with a layer of coarse sand, use the top-down infiltration direction to carry on the infiltration experiment and collect effluent liquid and determine the concentration of K⁺, Ca²⁺, Mg²⁺, SO₄²⁻. When the potassium concentration in leaching solution was not changed, stop the infiltration experiment and analysis of samples.

2.2.3 Analytical method

K⁺: sodium tetraphenylborate-quaternary ammonium salt antitipation; Ca²⁺, Mg²⁺: EDTA volumetric method; SO₄²⁻: EDTA—barium volumetric method.

3. Results and discussion

3.1. Results

The recovery of K⁺ from polyhalite was affected by the concentration of lixiviant, granularity of mineral, infiltration velocity of lixiviant and the length of infiltration route. The experiment results (Tab 1) indicate that the granularity of mineral is one of the most influencing factors to the recovery of K⁺ from polyhalite.

When the granularity of mineral is 2-3mm, the leaching rate of K⁺ can be 80.19% in 41h. When the granularity of mineral is 5-8mm, the
leaching rate of $K^+$ is only 42.17% in 71h.

Table 1. Effect of granularity of mineral to the leaching process of $K^+$

<table>
<thead>
<tr>
<th>size/mm</th>
<th>volume/L</th>
<th>$C_K$/g·L$^{-1}$</th>
<th>leaching rate of $K^+$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-3</td>
<td>0.2</td>
<td>5.118</td>
<td>9.40</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>5.802</td>
<td>25.39</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>5.442</td>
<td>40.38</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>3.172</td>
<td>52.03</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>2.198</td>
<td>62.13</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>1.297</td>
<td>68.08</td>
</tr>
<tr>
<td></td>
<td>2.9</td>
<td>0.771</td>
<td>73.04</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>0.649</td>
<td>77.21</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>0.541</td>
<td>80.19</td>
</tr>
<tr>
<td>5-8</td>
<td>0.2</td>
<td>2.739</td>
<td>5.03</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3.568</td>
<td>14.86</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>3.352</td>
<td>24.10</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>1.370</td>
<td>29.13</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>0.757</td>
<td>32.60</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>0.432</td>
<td>34.59</td>
</tr>
<tr>
<td></td>
<td>2.9</td>
<td>0.324</td>
<td>36.67</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>0.252</td>
<td>38.30</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>0.216</td>
<td>39.49</td>
</tr>
<tr>
<td></td>
<td>5.7</td>
<td>0.123</td>
<td>41.18</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>0.072</td>
<td>42.17</td>
</tr>
</tbody>
</table>

The results of the effect of the concentration of lixiviant, the length of infiltration route and the infiltration velocity are showed in figer 2 to figer 4. From them, it can be found that leaching rate and the concentration of $K^+$ increase with the concentration of the lixiviant and have a relationship with the length of infiltration route. The longer of the length of infiltration route, the higher of the concentration of $K^+$ ($C_K$) in lixiviant solution, and it can be up to 12.1g/L. It also shows that increasing the concentration of lixiviant and the length of infiltration route can raise the leaching velocity of $K^+$.

3.2 Mathematics simulation

3.2.1 Mathematics simulation theory

According to the dissolved heterogeneity reactive diffusion kinetic theory, water-soluble salts' infiltration leaching model [9] established by H.H.Веригин which is the earliest mathematical model to describe liquid-solid conversion process in mining. The water-soluble salts leaching process in the unidirectional infiltration was described in this model. The constant rate of the leaching process can be obtained quite simply from the leaching experiment results.

In the metal leaching process, the leaching agent reacts with ore mineral and certain rock forming minerals, and with the conditions changed, the dissolved metallic ion would be possibly precipitation in
the transportation process, and it would make this process more complex. В.С.Голубев, Г.Кричевц and other scientists [9] studied the metal unidirectional infiltration process in which the concentration of acid solution, counter-flow speed and the reaction of acid with gangue mineral were all considered. They modified and carried on the simplification to Н.Н.Веригин’s model and the following relationship is obtained:

\[ t_1 = \frac{q_0}{\gamma C_H} \]  
\[ v_k = \frac{U}{1 + \frac{m_0}{a_0}} \]  
\[ v_B = \frac{Uv_k C_H}{q_0 v_k + C_H U} \]

When \( v_B t \leq x \leq v_k t \) (at the area of metal leaching):

\[ C = C_H \left[ 1 - e^{-\frac{\gamma(x-v_B t)}{U-v_B}} \right] \]  
\[ q = C_H \left( \frac{U}{v_B} - 1 \right) \left[ 1 - e^{-\frac{\gamma(x-v_B t)}{U-v_B}} \right] \]

where: \( t_1 \)—the time of metal fully leaching to solution; \( \gamma \)—infiltration velocity constant; \( t \)—time; \( x \)—the length of infiltration route; \( U \)—infiltration velocity of lixiviant; \( v_k \)—velocity of acid; \( v_B \)—velocity of metal fully leaching; \( q_0 \)—original content of metal in solid phase; \( q \)—solid metal content in \( t \) time in solid phase; \( m_0 \)—other material original content.

In the above equation, the initial liquid concentration of metal is usually equal to zero, and \( C_H \) is decided by the leaching agent concentration \( (a_0) \). The metal leaching velocity of movement relies on the infiltration rate, which mainly relies on the leaching agent density. This model describes the metal dissolution behavior in the mining process.

In the leaching process of mining polyhalite, using CaCl₂ solution as the leaching agent is consistent with the mathematical model of chemistry leaching agent to dissolve metal. And the potassium component is soluble, the possibility of reprecipitation was unlikely to happen in the infiltration process, therefore, the metal leaching process was only considered in В.С.Голубев-Г.Н.Кричевц model.

In the model, \( C_H \) is defined as the original concentration of lixiviant. The parameters in the polyhalite leaching process are: \( q_0 \)—the original content of K⁺ in polyhalite; \( q \)—the remaining content of K⁺ in polyhalite; \( a_0 \)—the original concentration of CaCl₂; \( m_0 \)—the original content of Mg²⁺.
3.2.2 Mathematics simulation results

The relationship between the max concentration of $K^+$ and the length of infiltration route (fig 5 and fig 6) could be obtained from the figure 2 and figure 3, and from them it can be got that the max concentrations of $K^+$ ($C_{K,\text{max}}$) are 9.302g/L and 9.031g/L respectively. According to the above model, there was a linear relationship between the concentration of metal and the length of infiltration route in the formation of saturated solution ($C_H$, formula 4). According to date of figure 3 and figure 4, the curves between $\ln(1-C/C_H)$ and the length of infiltration route are obtained (fig 7 and fig 8), and the relevant coefficient are 0.9737 and 0.9888 respectively, it shows a good linear relationship.

According to formula 2 and formula 3, formula 6 can be obtained:

$$v_B = \frac{a_0 U C_H}{a_0 q_0 + a_0 C_H + C_H m_0}$$

(6)

And by the formula 5 and formula 6, formula 7 can be obtained:

$$\ln(1-\frac{C}{C_H}) = -\frac{a_0 q_0}{U(a_0 q_0 + C_H m_0)} \chi + \frac{a_0 C_H t}{a_0 q_0 + C_H m_0}$$

(7)

Where: $m_0$ is equal to 0.2799, $q_0$ is equal to 0.1481 and $a_0$ is equal to 0.4505.

According to the slope of rectilinear and experiential conditions ($m_0$, $q_0$, $a_0$), the parameters in the dynamic equation can be obtained and it is listed in table 2.
Table 2. The parameters in the dynamic equation

<table>
<thead>
<tr>
<th>Velocity /m·h⁻¹</th>
<th>Equation</th>
<th>γ/h⁻¹</th>
<th>U/m·h⁻¹</th>
<th>v₀/m·h⁻¹</th>
<th>v₁/m·h⁻¹</th>
<th>t₁/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.159</td>
<td>y = -3.15679x + 0.65779</td>
<td>0.278</td>
<td>0.159</td>
<td>0.07243</td>
<td>0.09806</td>
<td>2.233</td>
</tr>
<tr>
<td>0.318</td>
<td>y = -3.76609x + 0.65751</td>
<td>0.673</td>
<td>0.318</td>
<td>0.1406</td>
<td>0.1961</td>
<td>0.951</td>
</tr>
</tbody>
</table>

The results showed that the infiltration rate constant could improve from 0.278h⁻¹ to 0.673h⁻¹ and the time of metal fully leaching to solution decrease from 2.333h to 0.951h when the infiltration velocity increases from 0.159m/h to 0.318m/h. So increasing the infiltration velocity, it could raise the infiltration rate constant and decrease the time of metal fully leaching to solution.

3.3 Samples analysis before and after leaching

The analysis results of XRD and SEM of polyhalite are showed in figure 9 and figure 10. According to the references [10, 11], the polyhalite’s values of d of 5 feature diffraction in XRD are: 3.182(10), 2.929(8), 2.89(10), 2.854(5), 2.977(4) and 6.018(7), and the Gypsum’s values of d of 5 feature diffraction are 2.871(1), 4.28(0.9), 2.684(0.5). From the figure 9 (b), it can be seen the characteristic spectrogram of gypsum debris and the characteristic spectrum peak of polyhalite has vanished, it indicates that the conversion reaction of polyhalite in CaCl₂ solution is completed. By the SEM spectrogram, it can be found that the debris after leaching are very tiny and loose, it shows that compact solid product was not produced which would stopped the reaction of polyhalite with CaCl₂.

Fig.9. XRD spectrogram of polyhalite
4. Conclusions

Through the column infiltration experiment, it can be found that the granularity of mineral, the concentration of CaCl₂, infiltration velocity and infiltration route have the influence on recovery of K⁺. When granularity of mineral change from 2-3mm to 5-8mm, the recovery of K⁺ decreases from 80.19% to 42.17%; the recovery of K⁺ increase with the concentration of CaCl₂, infiltration velocity and infiltration route; the concentration of K⁺ in the leaching solution can be 12.1g/L higher in experiment.

The process of CaCl₂ solution to leaching polyhalite is conformable with the dynamic model of metal dissolving $C = C_H \left[ 1 - e^{-\frac{\gamma(x-vt)}{U-v^2}} \right]$, and there was an exponential relationship between the concentration of K⁺ and the ratio of infiltration velocity, infiltration route. When the infiltration velocity increases from 0.159m/h to 0.318m/h, the infiltration rate constant could improve from 0.278h⁻¹ to 0.673h⁻¹ and the time of metal fully leaching to solution from 2.333h to 0.951h.

Fig. 10. SEM spectrogram of polyhalite
Acknowledgements

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References