Simulation of one-dimensional column leaching of weathered crust elution-deposited rare earth ore

Ping LONG¹,², Guan-shi WANG³, Jun TIAN¹,⁴, Shi-li HU³, Si-hai LUO³

¹. School of Resources and Environmental Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China; ². Cooperative Innovation Center of Efficient Development and Application for Ionic Rare Earth Resources, Jiangxi University of Science and Technology, Ganzhou 341000, China; ³. School of Architectural and Surveying and Mapping Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China; ⁴. Institute of Applied Chemistry, Jiangxi Academy of Sciences, Nanchang 330029, China

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Abstract: The ion exchange model of the leaching process was determined via batch leaching experiments using the Kerr model, with the selectivity coefficient experimentally determined to be 12.59×10⁻¹⁰ L²/g². Solute transport laws of ammonium ions (NH⁴⁺) and rare earth ions (RE³⁺) in column leaching were described by the convection–dispersion equation (CDE). The source and sink in the CDE were determined by the Kerr model. The CDE with strong nonlinearity was solved using the sequential non-iterative method. Compared with the breakthrough curve of RE³⁺, the correlation coefficient between the simulated and experimental curves reached 0.8724. Therefore, this method can simulate the one-dimensional column leaching of weathered crust elution-deposited rare earth ore. Moreover, the effects of different concentrations of ammonium sulfate ((NH₄)₂SO₄) solution on the leaching rate of rare earth were analyzed. The optimal concentration of the (NH₄)₂SO₄ solution had a linear relationship with the rare earth grade.

Key words: weathered crust elution-deposited rare earth ore; column leaching; ion exchange; solute transport

1 Introduction

The basic process of the exploitation of weathered crust elution-deposited rare earth (RE) ore based on the in-situ leaching technique is as follows. First, ammonium sulfate ((NH₄)₂SO₄) solution is injected into the ore body via the injection well network. Second, ammonium ions (NH⁴⁺) in the (NH₄)₂SO₄ solution are used to exchange RE ions (assuming the average valence of RE ions is +3, RE³⁺), which are adsorbed onto clay particles and the RE³⁺ enters the solution. RE³⁺ moves with the solution until it flows out of the ore body and enters into the solution collection system [1−5]. The exchange of the solid-phase RE³⁺ (i.e., the RE³⁺ is adsorbed by clay particles) by the liquid-phase NH⁴⁺ (i.e., the NH⁴⁺ in solution) is a solid–liquid reversible ion exchange reaction [6,7]. The (NH₄)₂SO₄ concentration determines the exchange efficiency. Presently, the appropriate (NH₄)₂SO₄ concentration is usually estimated by experience. Owing to the complexity of geological conditions, different mines have different RE grades, permeabilities, and impurities of the ion content. Therefore, the concentration of the (NH₄)₂SO₄ solution determined by experience is often beyond the reasonable range. Too high a concentration of (NH₄)₂SO₄ will lead to excessive ammonia nitrogen in the surrounding water bodies, and thus environmental pollution. However, low concentrations will result in an insufficient leaching rate of RE and cause resource waste. Establishing a mathematical model for the leaching process provides theoretical reference for the reasonable determination of a suitable (NH₄)₂SO₄ concentration.

Leaching of RE ore primarily includes two processes: one is the RE³⁺ leaching (ion exchange process) and the other is the RE³⁺ transport (transport process). TIAN et al. [8−10] analyzed the ion exchange process of RE ore using the shrinking core model and...
found that the ion exchange process was controlled by inner diffusion. The leaching kinetics when using ammonium salt solution [11] and magnesium sulfate solution [12] as the leaching agents have also been studied, and researchers [13–15] have attempted to analyze the column leaching process with the leaching kinetic model. Studies [16–19] of ion exchange and the transport of RE\(^{3+}\) are mainly based on laboratory experiments; however, solute transport of RE\(^{3+}\) has a distinct scale effect and laboratory experimental results are often inapplicable to practical engineering. WU et al [20–22] elaborated on the ion exchange and transport mechanism in the heap leaching process, which provided direction for the theoretical analysis of leaching. QIU et al [23,24] simulated the leaching process of weathered elution-deposited RE ore using the lattice Boltzmann theory.

In the preset study, an ion exchange model of RE ore was obtained using batch leaching experiments. NH\(^4\) and RE\(^{3+}\) in the column leaching process were described by the convection–dispersion equation (CDE) and the source and sink of the CDE were determined by the ion exchange model. The feasibility of the proposed method was verified with a laboratory experiment. The proposed method was used to determine the optimal concentration of (NH\(_4\))\(_2\)SO\(_4\).

2 Experimental

2.1 Batch leaching experiments

Samples were collected from RE ore in Xinfeng County, Jiangxi Province, China, and were screened with a high-frequency sieve shaker having a sifter diameter of 2 mm. Screened mineral samples were baked for 10 h in 110 °C oven to eliminate water in the mineral samples. (NH\(_4\))\(_2\)SO\(_4\) solutions with different mass concentrations (2, 3, 4, 5, 6, 7 and 8 g/L) were prepared in volumetric flasks. Next, another seven iodine flasks were used to mix 20 g of mineral sample and 100 mL of (NH\(_4\))\(_2\)SO\(_4\) solution with different mass concentrations (2–8 g/L). These seven iodine flasks were first placed in a constant temperature (30 °C) water tank and vibrated for 2 h, and then remained static for 0.5 h. Leachate and mineral samples were separated by medium-speed filter paper and concentrations of RE\(^{3+}\) in the leachate were tested using the EDTA titration method. Three parallel experiments were performed.

2.2 Column leaching experiments

Column leaching experiments were performed with the mineral samples. The RE grade of the mineral samples was 0.101%. Length, radius, and porosity of the soil column were set at 0.80 m, 5.2 cm and 1.15%, respectively. The initial water content in the soil column was set to be 17.1%. The porous stone, which was wet with deionized water, was placed into a PVC tube with an inner diameter of 10.4 cm and a length of 1 m. One 1 cm-thick coarse sand filtering layer was paved and samples were filled in eight layers. Another 1 cm-thick coarse sand filtering layer was paved at the top of the soil column. A piece of overflow pipe was installed 5 cm above the coarse sand filtering layer and deionized water was added to the water tank. Water inflow in the PVC tube was controlled by a faucet. To control the height of ponding to be 5 cm, the velocity of the water inflow was fast enough to spill from the overflow pipe. After stabilization of the water flow in the soil column, the ponding at the top of the soil column was quickly extracted. Water in the water tank was changed into 20 g/L (NH\(_4\))\(_2\)SO\(_4\) solution. The ponding of the soil column quickly increased to 5 cm. The flow rate of the faucet was adjusted to maintain a constant head.

After replacement of the deionized water with the (NH\(_4\))\(_2\)SO\(_4\) solution, the mass of the leachate in the conical flask was weighed every 4 h (assuming the leachate density was 1 g/cm\(^3\)). Next, 10 mL leachate was added to oxalic acid. If no white precipitation was observed, this indicated that there was no RE\(^{3+}\) in the leachate. When RE\(^{3+}\) was detected in the testing solution, leachate was collected every 2 h thereafter. The concentration of RE\(^{3+}\) was tested using the EDTA titration method. The concentration of NH\(_4\) in the leachate was tested using the formaldehyde method. The concentration of sulfate ions (SO\(_4^{2-}\)) in the leachate was tested using the permanent white precipitation method. After the concentrations of RE\(^{3+}\), NH\(_4\) and SO\(_4^{2-}\) were stabilized close to zero, the experiment was stopped. The breakthrough curves of RE\(^{3+}\), NH\(_4\) and SO\(_4^{2-}\) were constructed.

3 Results and discussion

3.1 Ion exchange model

It is a solid–liquid ion exchange process for the liquid-phase NH\(_4\) to exchange the solid-phase RE\(^{3+}\). The Kerr model, Vanselow model, and Gapon model are common ion exchange models used to describe this solid–liquid ion exchange process. The expressions of the selectivity coefficients of these three models are as follows [25]:

\[
K_R = \frac{c_R^N (c_R^N)^3}{c_R^N (c_R^N)^3}
\]  
\[
K_V = \gamma_R \frac{M_R^3 c_R^N (M_R^N)^3}{\gamma_N c_N^N (M_N^N)^3}
\]
\[ K_G = \frac{(C_{lq}^R)^{1/3} C_{s}^N (M_{RE})^{2/3}}{3C_{lq}^R C_h^N} \]  

where \( K_K \), \( K_V \) and \( K_G \) are the selectivity coefficients of the Kerr model, Vanselow model, and Gapon model, respectively. \( C_h^N \) and \( C_{lq}^R \) refer to the concentrations of the liquid-phase NH\(_4\)+ and liquid-phase RE\(^{3+}\), respectively, g/L. \( C_s^N \) and \( C_s^R \) are the concentrations of the solid-phase NH\(_4\)+ and solid-phase RE\(^{3+}\), respectively, g/g. \( \gamma_N \) and \( \gamma_R \) are the activity coefficients of the liquid-phase NH\(_4\)+ and liquid-phase RE\(^{3+}\), respectively, which are calculated from the Davies empirical model (Eq. (4)). \( \bar{M}_s \) and \( \bar{M}_R \) are the molar fractions of the solid-phase NH\(_4\)+ and solid-phase RE\(^{3+}\), which are calculated using Eqs. (5) and (6), respectively. \( M_N \) and \( M_R \) are the relative molecular masses of NH\(_4\)+ and RE\(^{3+}\), respectively, g/mol.

\[
\lg \gamma = -Am^2 \left( \frac{\mu_s^{1/2}}{1 + \mu_s^{1/2}} - 0.3\mu \right)
\]

\[
\bar{M}_N = \frac{M_R C_s^N}{M_R C_s^N + M_N C_s^R}
\]

\[
\bar{M}_R = \frac{M_N C_s^N}{M_N C_s^N + M_R C_s^R}
\]

where \( A \) is the parameter related to the temperature, \( A = 0.513 \) (mol/L)\(^{-1/2} \) in 30 °C aqueous solution; \( m \) is the valence state of the corresponding ions; \( \mu \) is the ion strength.

Initially, there was no RE\(^{3+}\) in the liquid-phase and no NH\(_4\)+ was adsorbed during the solid-phase. Ions in the solid-phase and liquid-phase met the following three equality relations before and after the ion exchange process: (1) the amount of substance of solid-phase NH\(_4\)+ was 3 times that of the liquid-phase RE\(^{3+}\); (2) in the system composed of liquid-phase and solid-phase, NH\(_4\)+ and RE\(^{3+}\) met the law of mass conservation; (3) after ion exchange equilibrium, the sum of the amount of substance of the liquid-phase NH\(_4\)+ and solid-phase NH\(_4\)+ was equal to the amount of substance of the liquid-phase NH\(_4\)+ before leaching. These processes are expressed by Eqs. (7)−(9):

\[
C_N^s = \frac{3V_L M_N}{m_M C_{lq}^R}
\]

\[
C_{lq}^N = \frac{3M_N}{m_M} C_{lq}^R
\]

\[
C_s^R = \frac{C_{lq}^R}{m_s} V_L C_{lq}^R
\]

where \( m_s \) is the mass of the mineral sample, \( V_L \) is the volume of the solution, \( C_{lq}^0 \) is the concentration of NH\(_4\)+ in the leaching agent, and \( C_{lq}^R \) is the initial concentration of the solid-phase RE\(^{3+}\).

Substituting Eqs. (7)−(9) into Eqs. (1)−(3), the selectivity coefficients of the three models are the uniform functions of the concentration of liquid-phase RE\(^{3+}\). Given \( V_L/m_s \), \( C_{lq}^0 \), \( C_{lq}^R \), and \( C_{lq}^N \), the selectivity coefficients of the three models were calculated using the experimental data (Fig. 1).

The concentration of the liquid-phase RE\(^{3+}\) was obtained by leaching with different concentrations of (NH\(_4\))\(_2\)SO\(_4\), as shown in Fig. 1. Combined with the experimental data from Fig. 1, the selectivity coefficients of the three models under different (NH\(_4\))\(_2\)SO\(_4\) concentrations are shown in Fig. 2, where the selectivity coefficient of the Kerr model is amplified by 10\(^{10}\) times and the selectivity coefficient of the Vanselow model is amplified by 10\(^3\) times. The selectivity coefficient is often assumed to be constant. The mean selectivity coefficient under various (NH\(_4\))\(_2\)SO\(_4\) concentrations was calculated using data from Fig. 2. The selectivity coefficients of the Kerr model, Vanselow model, and Gapon model were calculated to be 12.59×10\(^{-10}\) L\(^2\)/g\(^2\).

![Fig. 1 Relationship between concentration of (NH\(_4\))\(_2\)SO\(_4\) and that of liquid-phase RE\(^{3+}\)](image)

![Fig. 2 Relationship between concentration of (NH\(_4\))\(_2\)SO\(_4\) and selectivity coefficients for Kerr model, Vanselow model and Gapon model](image)
The calculated selectivity coefficients of the three models were then substituted into Eqs. (1)−(9). The concentration of the liquid-phase RE$^{3+}$ was used as the basic unknown variable. The concentration of the liquid-phase RE$^{3+}$ under different (NH$_4$)$_2$SO$_4$ concentrations in the three models was calculated. The calculated results and experimental data are shown in Fig. 3. Relative errors and the mean of relative errors (Eq. (10)) between the calculated results for each model and experimental data are listed in Table 1. It was found that the relative errors of the Kerr model and Vanselow model are close and basically within 10.00% (although when the concentration of (NH$_4$)$_2$SO$_4$ was 2.0 g/L, the relative error of the Kerr model was 10.32%, which is slightly higher than 10.00%). The mean relative error of the Kerr model was slightly smaller than that of the Vanselow model. The calculation of the Gapon model deviated significantly from the experimental data under low concentrations of (NH$_4$)$_2$SO$_4$. The mean relative error of the Gapon model was more than twice that of the Kerr model and the Vanselow model, indicating that the Kerr model and the Vanselow model are better than the Gapon model. Compared to the Vanselow model and the Gapon model, the Kerr model had a lower mean relative error and a simpler mathematical expression. Therefore, the ion exchange process of leaching was described using the Kerr model. The selectivity coefficient of the Kerr model for the chosen mineral samples was 12.59×10$^{-10}$ L$^2$/g$^2$. The value of the selectivity coefficient for the Kerr model reflects the adsorption capacity of clays in terms of NH$_4^+$ and RE$^{3+}$. The mineral samples have a very small selectivity coefficient, indicating a significantly higher adsorption capacity of RE$^{3+}$ by clay particles than that of NH$_4^+$. If exchanging RE$^{3+}$ adsorbed on the clay surface by NH$_4^+$, then the concentration of NH$_4^+$ would be far higher than the concentration of RE$^{3+}$.

<table>
<thead>
<tr>
<th>Concentration of (NH$_4$)$_2$SO$_4$ (g·L$^{-1}$)</th>
<th>Kerr model</th>
<th>Vanselow model</th>
<th>Gapon model</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>10.32</td>
<td>3.88</td>
<td>37.56</td>
</tr>
<tr>
<td>3.0</td>
<td>0.83</td>
<td>3.49</td>
<td>12.25</td>
</tr>
<tr>
<td>4.0</td>
<td>6.26</td>
<td>6.90</td>
<td>1.07</td>
</tr>
<tr>
<td>5.0</td>
<td>3.91</td>
<td>3.51</td>
<td>3.51</td>
</tr>
<tr>
<td>6.0</td>
<td>0.79</td>
<td>2.15</td>
<td>2.11</td>
</tr>
<tr>
<td>7.0</td>
<td>1.09</td>
<td>2.94</td>
<td>4.05</td>
</tr>
<tr>
<td>8.0</td>
<td>4.15</td>
<td>6.15</td>
<td>2.78</td>
</tr>
</tbody>
</table>

Mean error 3.91 4.15 9.05

This is consistent with the research conclusions of LI [26] and CHI and TIAN [6].

$$\xi = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{C_{k,R}^{i} - \tilde{C}_{k,R}^{i}}{C_{k,R}^{i}} \right) \times 100\%$$

(10)

where $N$ is the experimental data number and $\tilde{C}_{k,R}^{i}$ is the experimental data for the liquid-phase RE$^{3+}$ concentration.

### 3.2 Hydrodynamic dispersion coefficient and mean flow velocity in pores

Mineral samples have low $SO_4^{2-}$ adsorption capacity in solution [27]. In the present study, $SO_4^{2-}$ was assumed to be a non-reactive solute and the transport of $SO_4^{2-}$ was described by the CDE. The approximation solution of the breakthrough curve of $SO_4^{2-}$ was expressed as per SAUTY [28]:

$$C_{k,S}^{S} = \frac{1}{2} C_{k,R}^{S} \text{erfc} \left( \frac{L - ut}{2\sqrt{Dt}} \right)$$

(11)

where erfc is the complementary error function, $C_{k,S}^{S}$ is the concentration of liquid-phase $SO_4^{2-}$, $C_{k,R}^{S}$ is the concentration of $SO_4^{2-}$ in the leaching agent, $L$ is length of the soil column, $u$ is the average flow velocity in pores, $D$ is the hydrodynamic dispersion coefficient, and $t$ is time.

In the case of a non-reactive solution and convection domination, the time corresponding to the breakthrough curve $C_{k,S}^{S}$ is the time for solute transport from the top to the bottom of the soil column, at the average flow velocity in pores [28], which is denoted as $t_{b,5}$. The average flow velocity in pores can be expressed as $u = L/t_{b,5}$. After infiltration in the column, the leaching experiment became stable, the water content in the soil column was 0.449. Breakthrough curves of RE$^{3+}$, $NH_4^+$, and $SO_4^{2-}$ are shown in Fig. 4, with $t_{b,5}$=5.26 d and the average flow velocity in the pores calculated as 0.152 m/d. Based on the least squares method, the
breakthrough curve of SO$_2^-$ was fitted using Eq. (11) and the hydrodynamic dispersion coefficient of the soil column was calculated as $8.88 \times 10^{-5}$ m$^2$/d.

The ion exchange process during leaching was described by the Kerr model. The relationship between the concentration of NH$_4^+$ and RE$^{3+}$ is expressed in Eq. (1). According to conservation of the adsorption sites on the mineral samples, there is

$$
\frac{C_s^N}{M_N} + \frac{3C_s^R}{M_R} = \frac{3C_{i0}^R}{M_R}
$$

(16)

Initially, the concentration of the solid-phase RE$^{3+}$ at any position in the soil column was equal to the concentration of the solid-phase RE$^{3+}$ before leaching, and the concentration of the solid-phase NH$_4^+$ at any position in the soil column was zero. At the bottom of the soil column, the concentration gradients of the solid-phase NH$_4^+$ and solid-phase RE$^{3+}$ were zero. Therefore, the boundary conditions for the solid-phase NH$_4^+$ and solid-phase RE$^{3+}$ were

$$
\begin{align*}
C_s^N &= 0 \ (t = 0, \ z > 0) \\
\frac{\partial C_s^N}{\partial z} &= 0 \ (t > 0, \ z = L) \\
C_s^R &= C_{i0}^R \ (t = 0, \ z > 0) \\
\frac{\partial C_s^R}{\partial z} &= 0 \ (t > 0, \ z = L)
\end{align*}
$$

(17, 18)

The equation set consisting of Eqs. (1), (12), (13) and (16) represents the solute transport equation for NH$_4^+$ and RE$^{3+}$ in the one-dimensional column leaching process. The solute transport equation of NH$_4^+$ and RE$^{3+}$ showed strong non-linearity. Under the boundary conditions of Eqs. (14), (15), (17) and (18), directly solving the solute transport equation requires abundant computer memory [29]. To avoid occupying a large amount of computer memory during computation, the transport process and ion exchange process were considered independently using the sequential non-iterative method [30,31]. First, $C_{i0}^N$ and $C_{i0}^R$ were calculated by the transport process. Second, the ion exchange process was considered to correct $C_{l0}^N$, $C_{l0}^R$, $C_s^N$ and $C_s^R$. The detailed calculation process is shown below.

The solute transport equation expressed by NH$_4^+$ and RE$^{3+}$, with sole consideration to the transport process (source and sink terms in Eqs. (12) and (13) were eliminated), was written in a differential form:

$$
\begin{align*}
C_{l0}^{N\uparrow} &= C_{l0}^{N\downarrow} + \frac{\Delta M}{\Delta z} \left( C_{l1}^{N\uparrow} - 2 C_{l0}^{N\downarrow} + C_{l1}^{N\downarrow} \right) - \frac{\Delta M}{2\Delta z} \left( C_{l1}^{N\uparrow} - C_{l1}^{N\downarrow} \right) \\
C_{l0}^{R\uparrow} &= C_{l0}^{R\downarrow} + \frac{\Delta M}{\Delta z} \left( C_{l1}^{R\uparrow} - 2 C_{l0}^{R\downarrow} + C_{l1}^{R\downarrow} \right) - \frac{\Delta M}{2\Delta z} \left( C_{l1}^{R\uparrow} - C_{l1}^{R\downarrow} \right)
\end{align*}
$$

(19, 20)
where \( k \) is the time nodes (\( k=0, 1, 2, \ldots, n_t-1, n_t \) is the total number of time nodes); \( i \) is the positional nodes (\( i=1, 2, 3, \ldots, n_p-1, n_p \) is the total number of positional nodes); \( \Delta t \) is the time step length; \( \Delta z \) is the positional step length.

The boundary conditions in Eqs. (14) and (15) were also expressed in differential form:

\[
\begin{align*}
C_{lq}^{N k 0} &= C_{lq 0}^N (k = 0, 1, 2, 3, \ldots, n_k) \\
C_{lq i 0}^N &= 0 (i = 1, 2, 3, \ldots, n_i) \\
C_{lq-i 0}^N &= C_{lq-i-2}^N (k = 0, 1, 2, 3, \ldots, n_k) \\
C_{lq}^R i 0 &= 0 (i = 0, 1, 2, 3, \ldots, n_i) \\
C_{lq-i 0}^R &= C_{lq-i-2}^R (k = 0, 1, 2, 3, \ldots, n_k)
\end{align*}
\]  

When \( k=0 \) and \( i=1 \), the values of \( C_{lq 0}^N \) and \( C_{lq 0}^R \) were obtained by Eq. (21) and are \( C_{lq 0}^N \) and 0, respectively. Substituting \( C_{lq 0}^N \) and \( C_{lq 0}^R \) into Eq. (19), the value of \( C_{lq 1}^{N i} \) was calculated. The process of transport and ion exchange affected the liquid-phase concentrations of \( \text{NH}_4^+ \) and \( \text{RE}^{3+} \). For discrimination, the concentrations of the liquid-phase \( \text{NH}_4^+ \) and the liquid-phase \( \text{RE}^{3+} \), with sole consideration to the transport process, were recorded as \( C_{lq 1}^{N i} \) and \( C_{lq 1}^{R i} \). The concentrations of the liquid-phase \( \text{NH}_4^+ \) and liquid-phase \( \text{RE}^{3+} \) with consideration to both the transport process and ion exchange process were recorded as \( C_{lq 2}^{N i} \) and \( C_{lq 2}^{R i} \). It can be seen from Eq. (22) that \( C_{lq 1}^{R i} \), \( C_{lq 2}^{R i} \), and \( C_{lq 2}^{N i} \) were all zero. Substituting them into Eq. (20), the value of \( C_{lq 2}^{R i} \) was then calculated.

The ion exchange process occurred at the same time. The concentration of \( \text{NH}_4^+ \) and \( \text{RE}^{3+} \) in the liquid-phase and solid-phase, at time level \( k+1 \) and position level \( i \), was described by the relationship in Eq. (1), which was rewritten into the discrete form as follows:

\[
K_K = \frac{C_{lq 2}^{R i k+1} (C_{lq 1}^{N i k+1})^3}{C_{lq 2}^{R i k+1} (C_{lq 1}^{N i k+1})^3} \tag{23}
\]

The difference between the mole number of the solid-phase \( \text{NH}_4^+ \) after ion exchange and the mole number before ion exchange was 3 times the difference between the mole number of the liquid-phase \( \text{RE}^{3+} \) after ion exchange and the mole number before ion exchange, expressed as

\[
C_{lq 2}^{R i k+1} = C_{lq 2}^{N i k+1} + \frac{3V_L M_N}{m_i M_R} \left( C_{lq 1}^{R i k+1} - C_{lq 1}^{R i k+1} \right) \tag{24}
\]

where \( C_{lq 1}^{R i k+1} \) is the liquid-phase \( \text{RE}^{3+} \) concentration at time level \( k+1 \) and position level \( i \) before ion exchange; \( m_i \) is the mass of mineral sample in the unit cell \( i \); \( m_i = \rho \pi r^2 \Delta z(1+e) \), \( \rho \) is the density of soil particles, \( e \) is the porosity and \( r \) is radius of the soil column; \( V_L \) is the volume of solution in the unit cell \( i \) and \( V_L = \pi r^2 \Delta z \theta \).

\( \text{NH}_4^+ \) and \( \text{RE}^{3+} \) met the law of mass conservation before and after ion exchange at position level \( i \). Therefore,

\[
C_{lq 2}^{N i k+1} = C_{lq 1}^{N i k+1} - \frac{3M_N}{M_R} \left( C_{lq 1}^{R i k+1} - C_{lq 1}^{R i k+1} \right) \tag{25}
\]

\[
C_{lq 2}^{R i k+1} = \left( C_{lq 1}^{R i k+1} - C_{lq 1}^{R i k+1} \right) \frac{V_L}{m_i} + C_{lq 2}^{R i k+1} \tag{26}
\]

where \( C_{lq 1}^{N i k+1} \) is the concentration of the liquid-phase \( \text{NH}_4^+ \) at time level \( k+1 \) and position level \( i \) before ion exchange.

The boundary conditions of the solid-phase \( \text{NH}_4^+ \) and \( \text{RE}^{3+} \) in Eqs. (17) and (18) were written in a differential form as follows:

\[
\begin{align*}
C_{lq 0}^{N i} &= 0 (i = 1, 2, 3, \ldots, n_i) \\
C_{lq k 0}^{R} &= C_{lq k-i-2}^{R} (k = 0, 1, 2, 3, \ldots, n_k) \\
C_{lq s 0}^{N} &= C_{lq s 1}^{N} (i = 1, 2, 3, \ldots, n_i) \\
C_{lq k s 0}^{R} &= C_{lq k s-i-2}^{R} (k = 0, 1, 2, 3, \ldots, n_k)
\end{align*}
\]  

When \( k=0 \) and \( i=1 \), the values of \( C_{lq 0}^{N i} \) and \( C_{lq 0}^{R i} \) were obtained from Eqs. (19)–(22). Given \( K_K, C_{lq 1}^{N i}, C_{lq 2}^{N i}, C_{lq 1}^{R i}, C_{lq 2}^{R i} \), substituting Eqs. (24)–(26) into Eq. (23), the nonlinear equation of \( C_{lq 2}^{R i} \) was obtained. This nonlinear equation was solved by the zero function in MATLAB. The calculated \( C_{lq 2}^{R i} \) was used in Eqs. (24)–(26) to calculate \( C_{lq 2}^{N i} \), \( C_{lq 1}^{N i} \) and \( C_{lq 2}^{R i} \). When \( k=0 \) and \( i=2 \), the boundary conditions were combined with the previous two steps. Similarly, \( C_{lq i 2}^{N i} \),


3.4 Optimization of ammonium sulfate solution

The breakthrough curve of RE$^{3+}$ under different concentrations of (NH$_4$)$_2$SO$_4$ was acquired using the proposed method, with the rest of the parameters remaining the same as those in the column leaching experiment. The breakthrough curves of RE$^{3+}$ under 5.0, 10.0 and 20.0 g/L concentrations of (NH$_4$)$_2$SO$_4$ are shown in Fig. 6. With the decrease in (NH$_4$)$_2$SO$_4$ concentrations, the peak concentration of the breakthrough curves of RE$^{3+}$ decreased, and the tailing phenomenon of the breakthrough curves became more obvious, combined with a longer leaching period and lower leaching rate of RE. The curves depicting the relationship between the concentration of (NH$_4$)$_2$SO$_4$ and the leaching rate of RE are shown in Fig. 7. For a given RE grade ($\eta$), the leaching rate of RE was positively related to the concentration of (NH$_4$)$_2$SO$_4$. There exists a concentration where the leaching rate of RE is constant after the concentration of (NH$_4$)$_2$SO$_4$ exceeds this concentration. This concentration is called the optimal concentration of (NH$_4$)$_2$SO$_4$ ($C_{op}^{NS}$). The curve for the relationship between $C_{op}^{NS}$ and $\eta$ is shown in Fig. 8, which showed a linear relationship. Based on linear fitting, $C_{op}^{NS}=10.19\eta$. Based on the relation equation between $C_{op}^{NS}$ and $\eta$, the consumption of (NH$_4$)$_2$SO$_4$
decreased under the premise of satisfying the leaching rate of RE. This offers theoretical reference for choosing the suitable concentration of (NH$_4$)$_2$SO$_4$ during RE exploitation using the in-situ leaching technique.

4 Conclusions

(1) Compared with the Vanselow model and Gapon model, the Kerr model was more suitable for describing the ion exchange process of RE leaching. The selectivity coefficient of the Kerr model was experimentally determined to be 12.59×10$^{-10}$ L$^2$/g$^2$.

(2) Using the Kerr model as the source−sink term, the transport process of RE$^{3+}$ in a one-dimensional soil column was simulated with the CDE model. The correlation coefficient between the simulated and experimental breakthrough curves of RE$^{3+}$ reached 0.8724, which indicates that the proposed method provides a good simulation of one-dimensional column leaching of weathered crust elution-deposited RE ore.

(3) The concentration of (NH$_4$)$_2$SO$_4$ was optimized by the proposed model. It was shown that the optimal concentration of (NH$_4$)$_2$SO$_4$ ($C_{op}^{NS}$) varied linearly with the RE grade ($\eta$). Under the conditions in the present study, the equation can be expressed as $C_{op}^{NS}$ = 10.19$\eta$.

References


风化壳淋积型稀土矿一维柱浸过程的模拟

1. 江西理工大学 资源与环境工程学院，赣州 341000；
2. 江西理工大学 江西省离子型稀土资源高效开发及应用协同创新中心，赣州 341000；
3. 江西理工大学 建筑与测绘工程学院，赣州 341000；
4. 江西省科学院 应用化学研究所，南昌 330029

摘 要：通过杯浸试验确定浸矿的离子交换模型为 Kerr 模型，得到 Kerr 模型的选择系数为 $1.59 	imes 10^{-10} \text{L}^2/\text{g}^2$；采用对流-弥散方程描述柱浸过程铵根离子和稀土离子的运动规律，通过 Kerr 模型确定对流-弥散方程中的源汇项，运用顺序非迭代法解具有强非线性的对流-弥散方程，模拟稀土离子在土柱中的运移过程。与室内一维柱浸试验稀土离子的穿透曲线进行比较，两者的相关系数达到 0.8724，说明本方法可以较为准确地模拟风化壳淋积型稀土矿一维柱浸过程。分析硫酸铵溶液浓度对稀土浸取率的影响，结果发现，最优硫酸铵溶液浓度($C_{NS}$)与稀土品位($\eta$)满足线性关系。

关键词：风化壳淋积型稀土矿；柱浸；离子交换；溶质运移

(Edited by Bing YANG)