Research Article

Effects of Concentration of Pore Solution on Stability of Ion-Absorbed Rare Earth Ore Aggregate

Jie Wang,1,2 Guanshi Wang,1 and Bengen Hong3

1School of Civil and Surveying and Mapping Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China
2College of Civil and Architectural Engineering, Panzhihua University, Panzhihua 617000, China
3Longyan Rare Earth Development Co. Ltd, Longyan 364000, China

Correspondence should be addressed to Bengen Hong;121903856@qq.com

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The continuous change in solution concentration in ore pores during in situ mineral leaching influences the stability of ore aggregate. In this study, influences of the concentration of ammonium sulfate (\(\text{(NH}_4\text{)}_2\text{SO}_4\)) solution on the interaction forces between ore particles were calculated. On this basis, the mechanism by which \(\text{(NH}_4\text{)}_2\text{SO}_4\) solution concentration influences the stability of ore aggregate was analyzed. Furthermore, an empirical formula for estimating the critical \(\text{(NH}_4\text{)}_2\text{SO}_4\) solution concentration for aggregation and dispersion of ore body aggregates with different grain composition was proposed. Some major conclusions were drawn. First, for ore bodies with an initial particle size of less than 0.075 mm, the interaction force between particles was net attraction, with the distance range of this force increasing as the concentration of \(\text{(NH}_4\text{)}_2\text{SO}_4\) solution increased from \(\leq 0.001\) to 0.16 mol·L\(^{-1}\), aggregation of ore particles occurring within this distance range. Secondly, for ore bodies with initial particle size of less than 0.075 mm, the interaction force between particles was net attraction, but with the distance range of this force decreasing when the \(\text{(NH}_4\text{)}_2\text{SO}_4\) solution concentration increased from 0.16 to 0.28 mol·L\(^{-1}\), dispersion of ore particles occurring beyond this distance range. Thirdly, for ore bodies with particle sizes of less than 0.038, 0.075 and 0.1 mm, the cation exchange capacity (CEC) was 9.13, 8.96, and 8.8 cmol·kg\(^{-1}\), respectively, and the critical \(\text{(NH}_4\text{)}_2\text{SO}_4\) solution concentration affecting the aggregation and dispersion of ore bodies was 0.12, 0.16, and 0.20 mol·L\(^{-1}\), respectively.

1. Introduction

Currently, researchers believe that failure of soil aggregate is due to three processes: expansion, explosion, and scattering [1, 2]. For a dry soil aggregate, soil particles are controlled by net attraction when the distance between soil particles is less than 1.5 nm [3, 4]. In this case, soil aggregate will generally not expand and scatter. When the drying soil aggregate is immersed into water, the distance between two adjacent soil particles increases quickly to 1.5 nm as a result of hydraulic repulsive force. This process is called the expansion process of soil aggregates [5]. Since the hydraulic repulsive force is a short-range force, its sphere of effective action is only 1.5 nm and soil aggregates do not scatter beyond this distance. When the distance between two adjacent soil particles is greater than 1.5 nm, electrostatic repulsion becomes the dominant force and it leads to a continuous increase in distance between soil particles, up to 30–60 nm. Small soil particles are released continuously. This process is called explosion and scattering of soil aggregates [6]. In these ways, Van der Waals forces, electrostatic repulsive force, and hydraulic repulsive force can significantly influence the interaction of soil particles in a water system, thus affecting the stability of soil aggregates [7–15].

For ion-absorbed rare earth ores, in situ mineral leaching is the preferred technique in China [16]. In this technique, ammonium sulfate solution is injected into the ore body through injecting holes, where it undergoes exchange reactions with rare earth ions. Rare earth ions enter the solution and form part of the mother liquor, which is then
2. Model Building

2.1. Calculation of the Interaction Forces among Ore Particles. Interaction forces between ore particles consist of the sum of electrostatic repulsive forces between ore particles. In other words, the interaction forces between ore particles are changed and the stability of the ore aggregate is affected. It affects the cohesion of ore body and further affects the strength of ore body and the stability of slope.

In this study, influences of \((\text{NH}_4)_2\text{SO}_4\) solution concentration on the thickness of the sliding layer in double-electrode layers on ore particle surfaces, and interaction forces of ore particles, were calculated under mixed electrolyte conditions. On this basis, the influencing mechanism of \((\text{NH}_4)_2\text{SO}_4\) solution concentration in ore pores on the stability of ore aggregate was determined.

2.2. Van der Waals Forces between Ore Particles. There is always mutual attraction between ore particles because there is always Van der Waals attraction between atoms or molecules at close range. Van der Waals forces between particles are dependent on the distance between particles and are expressed according to the following equation [17]:

\[
P_{\text{vdw}} = \frac{-A}{0.6\pi} (10 \, d)^{-3},
\]

where \(A\) is the Hamaker constant, with values of \(A\) for soil or clay in vacuum and in solution being \(12 \times 10^{-20} \text{J}\) and \(7.8 \times 10^{-20} \text{J}\), respectively. \(d\) is the distance between two adjacent particles.

2.3. Hydration Repulsion among Ore Particles. The hydration repulsion force is significantly stronger than the electrostatic repulsion force or Van der Waals force, but it acts over distances of only 1.5 nm. Thus, the hydration repulsion is a short-range acting force [18]. Based on experimental results, Leng [19] proposed that the hydration repulsion force (in atm) between two particles is proportional to the exponent of the distance between the two particles:

\[
P_h = 3.33 \times 10^{4} e^{-5.76 \times 10^3 d}.
\]

2.4. Electrostatic Repulsion between Ore Particles

2.4.1. Electrostatic Repulsion between Particles. Two ore particles were selected as the research objects. These were conceptualized as two plate-like viscous particles with uniform charge distribution on their surfaces. The surfaces of the plates were treated as planes that extend to infinity in the \(y\) and \(z\) directions; this assumption excludes fringe effects. It was assumed that the two particles equilibrate when the planes that represent the two particles are immersed in an electrolyte solution with a concentration of \(c_0\) at a mutual distance of \(d\). At equilibrium, the mutual repulsion of the double electric layers \((p_d)\) and the external pressure \((p_0)\) exerted by the two planes are equal (Figure 1).

The pressure on a unit volume within this space in the \(x\) direction is expressed as follows:

\[
F_x = \frac{dp}{dx}
\]

Unit volumes within this space are also subject to an electrostatic force, defined as the product of the charge density and the electric field intensity according to the following equation:

\[
F_e = \rho \frac{d\psi}{dx}
\]

The condition for equilibrium between the two particles is expressed as follows:

\[
\frac{dp}{dx} + \rho \frac{d\psi}{dx} = 0.
\]

Equation (6) can be rearranged to give

\[
dp = -\rho d\psi.
\]

The density is defined by equation (8), which can also be expressed as equation (9):

\[
\rho = \sum z_i F c_{i(0)} \exp \left( -\frac{z_i F \psi}{RT} \right),
\]

where \(F\) is the Faraday constant \((F = 96490 \text{C} \cdot \text{mol}^{-1})\), \(R\) is the universal gas constant \((R = 8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})\), \(T\) is the absolute temperature \((K\)), \(c_i\) is the ion concentration \((\text{mol-L}^{-1})\), the subscript 0 refers to the bulk solution, \(z_i\) is the ionic valence, and \(\psi(x)\) is the potential at \(x\) m from the particle surface \((V)\).

So,

\[
dp = -\sum z_i F c_{i(0)} \exp \left( -\frac{z_i F \psi}{RT} \right) d\psi.
\]

Therefore, \(p_R\) can be calculated using the following equation:

\[
p_R = p_d - p_0 = \int_{0}^{\psi(d/2)} -\sum z_i F c_{i(0)} \exp \left( -\frac{z_i F \psi}{RT} \right) d\psi = \sum z_i F c_{i(0)} \left\{ \exp \left( -\frac{z_i F \psi(d/2)}{RT} \right) - 1 \right\}.
\]
If the pressure is measured in atmospheres (1 atm = 101.325 kPa), then equation (10) becomes
\[
P_R = \frac{RT}{101} \sum_i c_{i(0)} \left\{ \exp \left( \frac{z_i F \psi (d/2)}{RT} \right) - 1 \right\}. \tag{11}
\]

2.4.2. Calculation of Potential on Ore Particle Surface.
According to equation (12), it is necessary to calculate the potential on the surface of the ore particles \( \psi_0 \) when calculating \( \psi (d/2) \). The method for calculating \( \psi_0 \) is explained below.

When the double layer in only the \( x \) direction is considered, and adsorption equilibrium is reached, the formula used to calculate the average ion concentration \( c_1 \) in diffusive double electric layers can be defined as follows [21]:
\[
c_1 = N_{\infty} = \frac{1}{V} \int_0^V c(x) \, dV = \kappa \int_0^{1/\kappa} c(x) \, dx, \tag{13}
\]

where \( N_{\infty} \) is the total area of adsorbed ions in the diffusion double layer, \( V \) is the total area of the diffusion double layer, \( 1/\kappa \) is the thickness of the double layer, and \( c(x) \) is the concentration of adsorbed ions from the surface of the solid particle to the distance \( x \). The expression for \( c(x) \) is given by
\[
c(x) = \sum_i c_{i(0)} \exp \left( \frac{-z_i F \psi}{RT} \right). \tag{14}
\]

Alternatively, \( c_1 \) can be calculated from
\[
c_1 = \frac{\text{CEC}}{S (1/\kappa)} = \frac{\text{CEC} \kappa}{S}, \tag{15}
\]

where CEC is the cation exchange capacity (cmol·kg\(^{-1}\)) and \( S \) is the specific surface area of particles (m\(^2\)·g\(^{-1}\)).

The potential at the center of the gap between the two particles, \( \psi (d/2) \), is expressed as follows [20]:
\[
\psi \left( \frac{d}{2} \right) = \frac{RT}{2} \pi \left[ 1 + \left( \frac{1}{2} \right)^2 \exp \left( \frac{2 i F \psi (d/2)}{RT} \right) + \left( \frac{3}{8} \right)^2 \exp \left( \frac{4 i F \psi (d/2)}{RT} \right) \right] - \arcsin \left[ \frac{\exp \left( \frac{Z_i F \psi (d/2)}{RT} \right)}{\epsilon RT} \right], \tag{12}
\]

Ultimately, equations (13) and (15) can be combined using a minimum error method to calculate the potential on the surface of ore particles \( \psi_0 \).

2.4.3. Calculation of \( \psi (x) \) on Ore Particle Surface.
When calculating the surface potential \( \psi_0 \) of ore particles, it is necessary to define the surface potential \( \psi(x) \). In order to calculate these two parameters, the diffusion double layer structure on the particle surface needs to be described mathematically. At present, the Guy–Chapman model is the most accepted method to achieve this, and it describes the double layer structure by the Poisson–Boltzmann equation. The nonlinear Poisson–Boltzmann equation for electrolyte solutions is expressed [22]:
\[
\frac{dy}{dx} = \sqrt{\frac{8 \pi \kappa F^2}{\epsilon RT} \sum_i c_{i (0)} \left[ \exp \left( -z_i \psi \right) - 1 \right]}, \tag{16}
\]

where \( \epsilon \) is the dielectric constant. The variable \( y \) is defined by \( y = F \psi(x)/RT \), where \( \psi(x) \) is the potential at \( x \) m from the particle surface \( V \).

When ammonium sulfate solution is injected into rare earth ores, ammonium ions in the solution exchange with rare earth ions on the surface of the ore particles. The solution surrounding the ore particles becomes a mixed electrolyte system. For these solutions, equation (16) becomes
where \( z_C, z_D, z_E, \) and \( z_H \) are the valences of the ammonium ions, the sulfate ions corresponding to ammonium ions, the rare earth ions, and the sulfate ions corresponding to rare earth ions, respectively; \( c_C, c_D, c_E, \) and \( c_H \) are the concentrations of the ammonium ions, the sulfate ions corresponding to ammonium ions, the rare earth ions, and the sulfate ions corresponding to rare earth ions, respectively.

With these substitutions, equation (17) becomes

\[
\frac{dy}{dx} = \sqrt{\frac{8\pi F^2}{eRT}} [c_C(e^{-2y} - 1) + c_D(e^{-z_Dy} - 1) + c_E(e^{-z_Ey} - 1) + c_H(e^{-z_Hy} - 1)],
\]

Setting \( y = y_0 \) at \( x = 0 \) and \( y = y(x) \) at \( x = x \), and rearranging, equation (18) becomes

\[
\int_{y_0}^{y(x)} \frac{1}{\sqrt{[c_C(e^{-2y} - 1) + 0.5c_C(e^{-3y} - 1) + c_E(e^{-3y} - 1) + 1.5c_E(e^{-2y} - 1)]}} dy = \int_0^x \sqrt{\frac{8\pi F^2}{eRT}} dx.
\]

Given that \( y = F\psi(x)/RT \), equation (19) can be substituted to produce the following equation for \( \psi(x) \):

\[
x_s = \frac{1}{\kappa_1} \ln \left( \frac{9c_E + 3c_C) - (6c_E + 2c_C)(1 - e^{F\psi(x)/RT}) + \sqrt{(6c_E + 2c_C)(1 - e^{F\psi(x)/RT}) - (9c_E + 3c_C)\left[1 - e^{F\psi(x)/RT}\right]^2 - (3c_E + c_C)^2}{\left[1 - e^{F\psi(x)/RT}\right]^2}} \right) \ln \left( \lambda_1 \right),
\]

Here, \( \lambda_1 \) and \( \kappa_1 \) are defined by equations (21) and (22), respectively.
2.5. Thickness of the Sliding Layer in Electric Double Layer. For rare earth ore bodies, when the concentration of \((\text{NH}_4)_2\text{SO}_4\) solution exceeds a certain level, ion exchange between the ammonium ions in solution and the rare earth ions on the surface of the ore particles occurs. This changes the ionic composition of the bulk solution around the ore particles and their surface potential, thus changing the thickness of the electric double layer on the surface of the particles. At present, the electric double layer thickness on the surface of particles can be approximately calculated by Debye parameter \(1/\kappa\), but this parameter only reflects the influence of the change in surface potential of particles caused by ion exchange. Ding proposed that the sliding layer thickness could be used to describe the electric double layer on the surface of particles [23]. Therefore, this section describes the method for calculating the sliding layer thickness in the double layer on the particle surface, which considers the influence of solution concentration and particle surface potential on the double layer thickness on the particle surface.

Equation (20) can be rearranged to obtain the following equation, an expression for the distance to the particle surface \((x)\):

\[
x_s = \frac{1}{\kappa_1} \ln \left( \frac{(9c_E + 3c_C) - (6c_E + 2c_C)(1 - e^{F/RT}) + \sqrt{(6c_E + 2c_C)(1 - e^{F/RT}) - (9c_E + 3c_C)^2} - (1 - e^{F/RT})^2 (3c_E + c_C)^2}}{(1 - e^{F/RT}) \lambda_i} \right)
\]

(23)

In electrolyte systems, \(\psi(x)\) in equation (20) can be equated with the value of the zeta potential \(\zeta\), so that \(x\) can be expressed in terms of the thickness of the sliding layer \((x_s)\), as shown in the following equation:

\[
x_s = \frac{1}{\kappa_1} \ln \left( \frac{(9c_E + 3c_C) - (6c_E + 2c_C)(1 - e^{F/RT}) + \sqrt{(6c_E + 2c_C)(1 - e^{F/RT}) - (9c_E + 3c_C)^2} - (1 - e^{F/RT})^2 (3c_E + c_C)^2}}{(1 - e^{F/RT}) \lambda_i} \right)
\]

(24)

3. Materials and Methods

3.1. Sample Preparation. Ionic clay rare earth ore was used as the test material in this study. The ionic clay was ground and screened using a 0.075 mm sieve. In order to analyze the effect of interaction between ore particles on the measured shear strength of the ore material, the total specific surface area and cation exchange capacity (CEC) of the samples were measured to enable the potential on the ore particle surfaces and the interaction forces between ore particles to be calculated. The total specific surface area was measured using a fully automated specific surface and pore diameter analyzer (Bates 3H-2000PS) utilizing a N₂-B.E.T method. The CEC was measured using an ammonium acetate exchange method.

3.2. Mineral Leaching Experiment Method. Raw ores, which were screened using a 0.075 mm sieve, were collected and \((\text{NH}_4)_2\text{SO}_4\) solution (0, 0.04, 0.08, 0.12, 0.16, 0.20, 0.24, and 0.28 mol·L\(^{-1}\)) was added. After thorough mixing, a controlled moisture content of 21.8% was reached throughout the sample. A cutting ring was used to form samples with a compaction density of 1.71 g·cm\(^{-3}\), diameter 6.18 cm, and height 2 cm. The ore samples were saturated in the cutting ring using the extraction saturation method. The saturation solution used the corresponding concentration of \((\text{NH}_4)_2\text{SO}_4\) solution and then the cutting ring was put in a 2 L beaker for mineral leaching at a solid to liquid ratio of 1:5. To enable enough time for adequate water-soil chemical reaction of the reshaped ore samples, and to prevent acid erosion of the ore cement by \((\text{NH}_4)_2\text{SO}_4\) solution, the reaction time was set to 1 day.

3.3. Ore Gradation Experiment Method. For raw ore with initial particle sizes of less than 0.075 mm, wet samples were tested in a laser particle analyzer (BT2002, China) after leaching in \((\text{NH}_4)_2\text{SO}_4\) solution. Each sample analysis was repeated at least five times.

3.4. Zeta Potential Test Method on Ore Particle Surfaces. A set of 0.5 g·L\(^{-1}\) mineral particle suspensions were prepared using four different concentrations of ammonium sulfate solution (0, 0.04, 0.08, 0.12, 0.16, 0.20, 0.24, and 0.28 mol·L\(^{-1}\)) and tested in a microelectrophoresis apparatus (JS94H2, China) without pH adjustment. The temperature was maintained at room temperature (25°C) during the test and each sample was tested at least five times. The error range on the measurements was ±2 mV.
4. Results and Discussion

4.1. Variation Law of Interaction Force between Ore Particles. Changes in solution concentration result in changes to the particle surface potential, the zeta potential, and the types of ions contained in the electric double layer. The thickness of double-electrode layers on ore particle surfaces and interaction forces between ore particles also change accordingly. To calculate the thickness of the sliding layer in the double-electrode layers on a particle surface and the interaction force between particles, ammonium ion concentration, rare earth ion (RE) concentration, zeta potential on an ore particle surface, CEC of ore sample, and specific surface area in solution with different concentrations of (NH₄)₂SO₄ solution after mineral leaching were determined. Main indexes of ore samples with initial particle size of less than 0.075 mm are shown in Table 1.

According to a previously reported theoretical calculation model, the concentration of bulk solution cannot be zero when calculating the interaction force between ore particles. Therefore, it is hypothesized that when the concentration of bulk solution is lower than a certain value, the zeta potential on ore particle surfaces does not change, and the electric double layer on the surface of ore body particles is not affected. In this study, (NH₄)₂SO₄ solution was used as the pore solution. The concentration of bulk solution was calculated to be approximately $2 \times 10^{-4}$ mol·L$^{-1}$ from equations (20)–(22) according to the zeta potentials when the concentration of (NH₄)₂SO₄ solution was 0 mol·L$^{-1}$.

Next, parameters were introduced into the ore particle surface potential calculation. The variation in particle surface potential when the (NH₄)₂SO₄ solution concentration increased from 0 to 0.28 mol·L$^{-1}$ was obtained. As can be seen from Figure 2, particle surface potential decreased from −372 to −126 mv when the (NH₄)₂SO₄ solution concentration increased from 0 to 0.28 mol·L$^{-1}$. This was mainly due to the negatively charged particles with one double-electrode layer absorbed on the particle surfaces, resulting in a relatively low initial concentration of ions in the double-electrode layer. With increasing (NH₄)₂SO₄ concentration in the ore pores, the concentration difference drove the movement of ammonium ions in the pore solution towards the double-electrode layer adsorbed onto the soil particle surfaces and then gradually through the double-electrode layer. In addition to ion exchange between some ammonium ions and rare earth ions, some ammonium ions were finally adsorbed on the ore particle surfaces and neutralized negative charges on the ore particles. This decreased the charge of ore particles and the soil particle surface potentials. This research conclusion was consistent with Liu’s [24].

4.1.1. Calculation of Thickness of Sliding Layer on Ore Particle Surface. Given the zeta potential on the particle surfaces and the calculated surface potential, the thickness of the sliding layer in the double-electrode layer on the particle surfaces could be calculated using equation (24). The results are shown in Figure 3. The thickness of the sliding layer decreased from 43.50 to 3.00 nm, when the (NH₄)₂SO₄ solution concentration increased from 0 to 0.16 mol·L$^{-1}$, and from 3.00 to 3.47 nm, when the (NH₄)₂SO₄ solution concentration increased from 0.16 to 0.28 mol·L$^{-1}$.

4.1.2. Calculation of Electrostatic Repulsive Force between Ore Particles. With the particle surface potentials now known, variation in the electrostatic repulsion force between particles at different (NH₄)₂SO₄ solution concentrations could be calculated using equation (10). Results are shown in Figure 4.

It could be seen from Figure 4 that the electrostatic repulsive force between two fixed ore particles was negatively correlated to the (NH₄)₂SO₄ solution concentration between 0.04 and 0.16 mol·L$^{-1}$ but was positively correlated from 0.16 to 0.28 mol·L$^{-1}$. For the electrostatic repulsive force between two fixed ore particles, the main influencing factors included solution concentration and thickness of double electric layer on particle surface [25]. Thus, the variation of electrostatic repulsive force in Figure 4 could be analyzed as follows.

First, when the (NH₄)₂SO₄ solution concentration was lower than 0.16 mol·L$^{-1}$, there was a negative correlation with the electrostatic repulsive force between ore particles. The existence of an electrostatic repulsive force between particles means there must be an overlap of the double electric layer on the two particle surfaces. Given that there is a certain number of ions in the double-electrode layer, this number of ions increases with expansion of the overlapping area and the electrostatic repulsive force between particles also increases (shadowed areas in Figure 5(a)). According to calculations, the thickness of the sliding layer on the ore particle surface decreased from 43.50 to 3.00 nm when the (NH₄)₂SO₄ solution concentration increased from 0 to 0.16 mol·L$^{-1}$; in other words, although the number of ions in the double electric layer on the particle surfaces increased with increasing (NH₄)₂SO₄ solution concentration, the thickness of the double-electrode layer decreased and the overlapping region of the double electric layer between two particles became narrower (Figure 5(b)). The net result was a decrease in electrostatic repulsive force between ore particles.

Secondly, when the (NH₄)₂SO₄ solution concentration was greater than 0.16 mol·L$^{-1}$, the electrostatic repulsive force between particles was positively correlated with concentration. As the (NH₄)₂SO₄ solution concentration increased from 0.16 to 0.28 mol·L$^{-1}$, the thickness of the sliding layer increased from 3.00 to 3.47 nm. In other words, the thickness of the double electric layer on the particle surfaces increased with increasing (NH₄)₂SO₄ solution concentration and the overlapping area expanded. Furthermore, the number of ions in the double electric layer on the particle surfaces increased accordingly. Therefore as shown in Figures 5(b) and 5(c), the net result was an increase in the electrostatic repulsive force between ore particles.

4.1.3. Calculation of Net Force between Ore Particles. When the surface potential is known, the variation in net force between ore particles at different (NH₄)₂SO₄ solution concentrations...
concentrations can be calculated using equation (1). Results are shown in Figure 6.

Figure 6 shows that when the (NH₄)₂SO₄ solution concentration was \( \leq 0.001 \text{mol} \cdot \text{L}^{-1} \), the distance between particles ranged from 1.55 to 1.75 nm; when the (NH₄)₂SO₄ solution concentration was 0.08 mol \cdot L^{-1}, the distance between particles ranged from 1.55 to 2.70 nm; when the (NH₄)₂SO₄ solution concentration was 0.16 mol \cdot L^{-1}, the distance between particles ranged from 1.55 to 3.00 nm; when the (NH₄)₂SO₄ solution concentration was 0.24 mol \cdot L^{-1}, the distance between particles ranged from 1.55 to 3.00 nm; and when the (NH₄)₂SO₄ solution concentration was 0.28 mol \cdot L^{-1}, the distance between particles ranged from 1.55 to 2.90 nm.

Additionally, Figure 6 shows that when the (NH₄)₂SO₄ solution concentration ranged from 0.04 to 0.28 mol \cdot L^{-1}, the net force between ore particles transformed from net repulsion to net attraction when the distance between two particles increased; this net attraction reached a maximum at approximately 1.55 nm. When the (NH₄)₂SO₄ solution concentration ranged from 0.04 to 0.16 mol \cdot L^{-1}, the maximum net attraction was positively correlated with the (NH₄)₂SO₄ solution concentration. In contrast, the maximum net attraction was negatively correlated with the (NH₄)₂SO₄ solution concentration from 0.16 to 0.28 mol \cdot L^{-1} (Figure 7).

4.2. Effects of (NH₄)₂SO₄ Solution Concentration on the Stability of Ore Aggregate

4.2.1. Determining the Critical (NH₄)₂SO₄ Solution Concentration at Particle Size Less Than 0.075 mm.

Table 1: Main indexes of ore samples with initial particle size of less than 0.075 mm.

| Sample no. | Ammonium ion concentration (mol \cdot L^{-1}) | RE concentration (mol \cdot L^{-1}) | Zeta potential on particle surface (mv) | Specific surface area of particles (m²·g⁻¹) |
|------------|---------------------------------------------|------------------------------------|----------------------------------------|---------------------------------------------|
|            | Before                                      | After                              |                                        |                                             |
| 1          | \leq 0.001                                  | 0                                  | -42.25                                 | 23.87                                       |
| 2          | 0.08                                        | 0.078                              | -34.20                                 | 19.99                                       |
| 3          | 0.16                                        | 0.154                              | -31.10                                 | 18.14                                       |
| 4          | 0.24                                        | 0.224                              | -27.45                                 | 18.57                                       |
| 5          | 0.32                                        | 0.308                              | -25.25                                 | 17.57                                       |
| 6          | 0.40                                        | 0.383                              | -15.50                                 | 18.54                                       |
| 7          | 0.48                                        | 0.46                               | -10.40                                 | 17.54                                       |
| 8          | 0.56                                        | 0.531                              | -7.60                                  | 18.65                                       |

Figure 2: Relationship between (NH₄)₂SO₄ solution concentration and particle surface potential.

Figure 3: Variation of sliding layer thickness on ore particle surfaces.

4.2. Effects of (NH₄)₂SO₄ Solution Concentration on the Stability of Ore Aggregate

4.2.1. Determining the Critical (NH₄)₂SO₄ Solution Concentration at Particle Size Less Than 0.075 mm.

Particle grading curves of ore bodies at different (NH₄)₂SO₄ solution concentrations were determined. A shown in Figure 8(a), the content of fine particles (<50 μm) decreased while the content of larger particles (>50 μm) increased when the (NH₄)₂SO₄ solution concentration was 0.12 mol \cdot L^{-1}, the distance between particles ranged from 1.55 to 2.90 nm; when the (NH₄)₂SO₄ solution concentration was 0.16 mol \cdot L^{-1}, the distance between particles ranged from 1.55 to 3.05 nm; when (NH₄)₂SO₄ solution concentration was 0.20 mol \cdot L^{-1}, the distance between particles ranged from 1.55 to 3.00 nm; and when the (NH₄)₂SO₄ solution concentration was 0.28 mol \cdot L^{-1}, the distance between particles ranged from 1.55 to 2.90 nm.

Changes in the interaction forces between ore particles determine the clustering or scattering behavior of particles. Therefore, the influences of (NH₄)₂SO₄ solution concentration
on clustering of ore particles were explained on the basis of the interaction forces between ore particles described in Section 3.1, with further details provided below.

First, when the (NH₄)₂SO₄ solution concentration was lower than the critical concentration, ore particles clustered gradually with increasing (NH₄)₂SO₄ solution concentration. According to the calculated interaction force, the interaction force between particles became net attraction when the (NH₄)₂SO₄ solution concentration was ≤0.001 mol·L⁻¹ and the distance between ore particles was within 1.55–1.75 nm, resulting in ore particles in this distance range clustering together, while ore particles beyond

**Figure 4:** Relationship between electrostatic repulsive force and distance between two particles. (a) ≤001~0.16 mol/L (NH₄)₂SO₄ solution. (b) 0.16~0.28 mol/L (NH₄)₂SO₄ solution.

**Figure 5:** Diagram of variations in double electric layer on particle surfaces at different concentrations of (NH₄)₂SO₄ solution. (a) 0.04 mol·L⁻¹. (b) 0.16 mol·L⁻¹. (c) 0.28 mol·L⁻¹. Notes: yellow solid dots are soil particles, red solid dots are cations, and black circles show the double-electrode layer adsorbed onto the particle surface.
this distance range did not. Similarly, the interaction force between particles was net attraction when the (NH₄)₂SO₄ solution concentration was 0.04, 0.08, 0.12, and 0.16 mol·L⁻¹ and the distance between ore particles was 1.55–2.70, 1.55–2.80, 1.55–2.90, and 1.55–3.05 nm, respectively. This indicated that ore particles clustered into aggregates in these three distance ranges. Therefore, the distance range of net attraction increased when the (NH₄)₂SO₄ solution concentration increased from ≤0.001 to 0.16 mol·L⁻¹ and ore particles within this distance gradually agglomerated into new aggregates, as shown in Figure 8(a) [26, 27].

Secondly, when the (NH₄)₂SO₄ solution concentration was higher than the critical concentration, ore particles scattered with increasing (NH₄)₂SO₄ solution concentration. According to calculations, the interaction force between particles was net attraction at four (NH₄)₂SO₄ solution concentrations (0.16, 0.20, 0.24, and 0.28 mol·L⁻¹) and four corresponding distance ranges (1.55–3.5, 1.55–3.00, 1.55–3.00, and 1.55–2.90 nm). In other words, ore particles clustered into aggregates in these distance ranges. Therefore, the distance range of net attraction decreased when (NH₄)₂SO₄ solution concentration increased from 0.16 to 0.28 mol·L⁻¹ and ore particles beyond this distance were gradually dispersed, as shown in Figure 8(b) [26, 27].

4.2.2. Effects of CEC on Critical (NH₄)₂SO₄ Solution Concentration. Based on the above analysis, for ore bodies with particle sizes of less than 0.075 mm, the critical (NH₄)₂SO₄ solution concentration affecting aggregation and dispersion of ore particles was determined and the relevant mechanism elucidated. Ore grading after mineral leaching for different particle sizes (0.038 and 0.1 mm) and different (NH₄)₂SO₄ solution concentrations was performed according to the experimental method described in Section 2.1. The results are shown in Figures 9 and 10.
Figures 9 and 10 reveal that the critical (NH₄)₂SO₄ solution concentration was 0.20 mol·L⁻¹ for particles smaller than 0.038 mm and 0.12 mol·L⁻¹ for particles smaller than 0.1 mm. According to calculations of the interaction force between ore particles, solution concentration was the main influencing factor. Therefore, changes in the critical (NH₄)₂SO₄ solution concentration arising from different grading levels was related to changes in CEC, thus influencing changes to the concentration of solution surrounding ore particles [28, 29]. Therefore, the relationship between CEC and critical concentration of (NH₄)₂SO₄ solution was further analyzed (Figure 11).

It can be seen from Figure 11 that there was an exponential relationship between critical (NH₄)₂SO₄ solution concentration and CEC of ore particles: 

\[ c_{\text{cri}} = a + b \exp(\text{CEC}/c) \]

where \( c_{\text{cri}} \) is the critical concentration of (NH₄)₂SO₄ solution, CEC is the cation exchange capacity on the ore particle surface, and \( a, b, \) and \( c \) are fitting parameters \((a = 0.058, \ b = 5.18 \times 10^{-11}, \) and \( c = 0.42)\). The critical (NH₄)₂SO₄ solution concentration can be estimated when
the CEC is fixed; on this basis, critical concentrations of (NH₄)₂SO₄ solution at different particle compositions could be determined.

5. Conclusions

For ion-absorbed rare earth ores, the concentration of the injected (NH₄)₂SO₄ solution in in situ mineral leaching is generally no higher than 0.23 mol·L⁻¹. And due to the ion exchange effect, interaction forces between ore particles are changed. This changes the stability of the ore body aggregates, and the particles are aggregated or diffused, which directly affects the cohesive force of the ore body and thus affects the shear strength and stability of the ore body slope. At the same time, the agglomeration or diffusion of ore body particles will directly affect the effective diameter of the pores in the ore body, thus affecting the permeability and directly affecting the mining efficiency. Therefore, the effect of (NH₄)₂SO₄ solution concentration on the interaction force between ore particles was calculated and the mechanism underpinning the effect of (NH₄)₂SO₄ solution concentration on ore aggregate stability was determined. Ultimately, an empirical formula for estimating the critical (NH₄)₂SO₄ solution concentration for aggregation and dispersion of ore body aggregates at different grain compositions was proposed. Some major conclusions could be drawn, which can provide reference for the concentration selection of ammonium sulfate solution in the leaching and mining process of ammonium sulfate solution in different gradation ionic rare earth mines.

(1) For ore bodies with initial particle size smaller than 0.075 mm, when the (NH₄)₂SO₄ solution concentration was ≤0.001 mol·L⁻¹, the interaction force between ore particles was net repulsion resulting in ore particle dispersion. The interaction force between particles was net attraction at four (NH₄)₂SO₄ solution concentrations of 0.04, 0.08, 0.12, and 0.16 mol·L⁻¹ and the four corresponding distance ranges of 1.55–2.70, 1.55–2.80 nm, 1.55–2.90 nm, and 1.55–3.05 nm, resulting in ore particle clustering into aggregates within these distance ranges. Therefore, the net attraction distance range increased when the (NH₄)₂SO₄ solution concentration increased from ≤0.001 to 0.16 mol·L⁻¹, resulting in the aggregation of ore particles within this range.

(2) For ore bodies with initial particle size of less than 0.075 mm, the interaction force of particles was net attraction at four (NH₄)₂SO₄ solution concentrations of 0.16, 0.20, 0.24, and 0.28 mol·L⁻¹ and the four corresponding distance ranges of 1.55–3.05, 1.55–3.00, 1.55–3.00, and 1.55–2.90 nm, with ore particles clustering into aggregates in these distance ranges. Therefore, the net attraction distance range decreased with increasing (NH₄)₂SO₄ solution concentration from 0.16 to 0.28 mol·L⁻¹, with the dispersion of ore particles beyond the range of net attraction.

(3) For ore bodies with particle sizes of less than 0.038, 0.075, and 0.1 mm, the CEC was 9.13, 8.96, and 8.8 cmol·kg⁻¹, respectively. The critical (NH₄)₂SO₄ solution concentration that discriminated between clustering and scattering of ore particles was 0.12, 0.16, and 0.20 mol·L⁻¹, respectively. Therefore, there was an exponential correlation between the critical (NH₄)₂SO₄ solution concentration and CEC.

Notations

- \( \rho \): Interaction forces between ore particles
- \( \rho_R \): Electrostatic repulsion
- \( \rho_h \): Hydration repulsion
- \( \rho_{vdw} \): Van der Waals forces
- \( A \): Hamaker constant
- \( d \): The distance between two adjacent particles
- \( c_0 \): Concentration of electrolyte solution
- \( P_d \): The mutual repulsion of the double electric layers
p_0: The external pressure
F: Electrostatic force
F_0: Faraday constant (F = 96490 C·mol⁻¹)
R: Universal gas constant (R = 8.314 J·mol⁻¹·K⁻¹)
T: Absolute temperature (K)
c: Concentration of adsorbed ions from the surface of
(x): W thickness of the double layer
1/κ: Thickness of the double layer
V: Total area of the diffusion double layer;
c(x): Concentration of adsorbed ions from the surface of the solid particle to the distance x
ψ(x): Potential at x m from the particle surface (V)
N: Total area of adsorbed ions in the diffusion double layer
ζ: Zeta potential
S: Specific surface area of particles (m²·g⁻¹)
Z_c: The valences of the ammonium ions
Z_SO_4: The valences of the sulfate ions corresponding to ammonium ions
Z_IR: The valences of the rare earth ions
Z_SO_4: The valences of the rare earth ions corresponding to rare earth ions
c_Am: The concentrations of the ammonium ions
C_SO_4: The concentrations of the sulfate ions corresponding to ammonium ions
C_IR: The concentrations of the rare earth ions
C_SO_4: The concentrations of the sulfate ions corresponding to rare earth ions
ξ: Zeta potential
x_s: The thickness of the sliding layer.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare no conflicts of interest.

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