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Seepage process on weathered crust elution-deposited rare earth ores with ammonium carboxylate solution

Hualiang Zou ¹, Zhenyue Zhang ^{1,2}, Zhuo Chen ¹, Defeng Liu ¹, Xiuwei Chai ¹, Han Zhang ¹, Ru-an Chi ^{1,2}

¹ School of XingFa Mining Engineering, Wuhan Institute of Technology, 430073, Wuhan, Hubei, China

² Key Laboratory for Green Chemical Process of Ministry of Education, Wuhan Institute of Technology, 430073, Wuhan, Hubei, China

Corresponding author: zyzxm@126.com (Zhenyue Zhang)

Abstract: In order to reveal the seepage law of ammonium carboxylate solution in the in-situ leaching process of weathered crust elution-deposited rare earth ores, the effects of concentration, pH, temperature, particle size and porosity on permeability were discussed in this paper. The results shown that the seepage of the leaching agent solutions in the rare earth ore follows Darcy's law and displays a laminar flow under the conditions of this experiment and seepage velocity can be increased by changing leaching conditions. The permeability coefficients are inversely proportional to concentrations of ammonium acetate, ammonium tartrate and ammonium citrate whose concentration is greater than 0.7wt%, because the insoluble complexes formed by the reaction of ammonium citrate with RE³⁺ at lower concentration decrease the permeability coefficient. The permeability coefficients of ammonium carboxylate solutions increase firstly and then decrease with the pH increased. The maximum of permeability coefficients of ammonium acetate, ammonium tartrate and ammonium citrate solution were 2.92, 1.91 and 2.70, respectively, while the pH of solution were 5, 6 and 7, respectively. Increasing temperature is beneficial for the seepage of ammonium carboxylate solution in orebody, therefore, it is helpful for leaching operation in summer. Moreover, clay minerals particle size and porosity are the key factors affecting the permeability of ammonium carboxylate solution in orebody. The permeability coefficients of ammonium acetate, ammonium tartrate and ammonium citrate solutions are 2.92×10^{-4} cm/s, 1.90×10^{-4} cm/s and 2.69×10^{-4} cm/s, respectively, at the same temperature of 293K, original particle size and porosity of the ore. Ammonium acetate solution has the best permeability in orebody.

Keywords: permeability, weathered crust elution-deposited rare earth ore, ammonium carboxylate, hydrodynamics

1. Introduction

Weathered crust elution-deposited rare earth ores were firstly discovered and utilized for industry in China which are rich in medium and heavy rare earth, where widely distributed in the seven provinces of Jiangxi, Guangdong, Fujian, Guangxi, Yunnan, Hunan and Zhejiang in south China (Zhang et al., 2016; Zhang et al., 2018). Rare earth elements (REEs) are mainly adsorbed on clay minerals in the forms of hydrated ions or hydroxyl hydrated ions in weathered crust elution-deposited rare earth ores, which can be exchanged with cations in leaching agent solution and then eluted with the solution. At present, the main leaching process of weathered crust elution-deposited rare earth ores is in-situ leaching, and ammonium salts are the main leaching agents to exchange rare earth elements from the ores. Under the actions of gravity potential, capillary potential, macro pressure potential etc, the leaching agent solution permeates slowly into the rare earth ores (He et al., 2017). Leaching rate of rare earth is mainly depended on the exchange capacity of rare earth ions with cations in leaching agent solution and the permeability of the leaching agent solution in rare earth ores. The ion exchange reaction is usually conducted as a

fast process, and then the permeability should be the vital factor determined the leaching rate of RE ores (Liu et al., 2009). Moreover, the permeability of solution in rare earth ore also plays a crucial role in the stability of the ore slope and collection system in the leaching technology (Wu et al., 2005). Therefore, it will be important to investigate the seepage process of weathered crust elution-deposited rare earth ore to improve its permeability. In addition, the characteristics of clay mineral in the weathered crust elution-deposited rare earth ores include large specific surface area, small-size mineral particle, small porosity and formation of electric double layer in pores. It will decrease the permeability of rare earth ore and the rate of leaching (Zuo et al., 2007). Therefore, strengthening the permeability of leaching agent solution is helpful to improve leaching rate of REEs and shorten the period of leaching process. That is why many studies have been carried out by domestic and foreign scholars, and have some positive outcomes.

Previous studies on the permeability of weathered crust elution-deposited rare earth ores were mainly focused on inorganic ammonium salts, such as ammonium chloride, ammonium sulfate, ammonium nitrate, etc. However, there are some limitations in ammonium salts, such as higher concentration up to 2.50 wt.%, lower leaching rate of HREEs and higher content of impurity (Chen et al., 2018; Li et al., 2017). Moreover, inorganic ammonium salt solution was easily to cause swelling of clay minerals from weathered crust elution-deposited rare earth ores and increased the possibility of landslides. (Li et al., 2017). As novel lixiviant, there are some advantages in leaching process of rare earth while used ammonium carboxylate solution, including higher leaching rate of REEs, lower impurity of leaching solution and so on. However, the mechanisms of adsorption and desorption of ammonium carboxylate in weathered crust elution-deposited rare earth ore are complex. The interactions between organic ions and clays are mainly determined by coordination reaction, double-layer theory and surface tension. Therefore, it is necessary to investigate the seepage rules of ammonium carboxylate leaching solution in weathered crust elution-deposited rare earth ores.

In this paper, the permeability was investigated on the physicochemical properties of fluid and rare earth ore. The effects of solution properties, including concentration, pH and temperature were discussed. Meanwhile, the effects of rare earth ore properties, such as particle size and porosity of weathered crust elution-deposited rare earth ore were conduct. Then it will conducive to not only revealing the seepage rules, but also explaining the interaction mechanisms between ammonium carboxylate and weathered crust elution-deposited rare earth ore. This work has guiding significances for industrial application of ammonium carboxylate leaching agent.

2. Materials and methods

2.1. Materials and characterization

The rare earth ore samples used in this experiment were collected from weathered crust elution-deposited rare earth ores in Myanmar. Its main chemical compositions were analysed by XRF. The result was shown in Table 1.

Table 1 Main chemical composition of the RE ores (%)

Component	REO	Al ₂ O ₃	MnO ₂	ZnO	CaO	MgO	K ₂ O	SiO ₂
content	0.12	21.12	0.01	0.01	0.02	0.88	3.94	66.25
Component	SO ₃	TiO ₂	Fe ₂ O ₃	Rb ₂ O	SrO	ZrO ₂	BaO	Loss
content	0.31	1.90	6.75	0.01	0.07	0.07	0.04	7.45

The sample contains 66.25% SiO₂ and 21.12% Al₂O₃, indicating that weathered crust elution-deposited rare earth ores are mainly composed of quartz and clay minerals.

The rare earth sample of different particle sizes was weighed respectively after screening the rare earth ore sample by sieves with different apertures, and the result was shown in Fig. 1 (the accumulative distribution curve of particle size).

The permeability of ore is related to its properties, and is proportional to the quadratic of ore inter

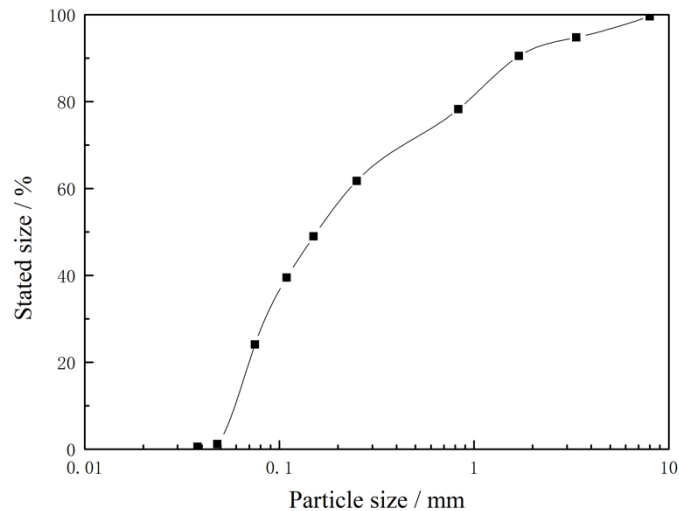


Fig. 1. Accumulative distribution curve of particle size

space size (d_0), $k = \frac{\gamma}{32\mu} \cdot d_0^2 \cdot n$ (Bouffard and Dixon, 2001). As it can be seen from Fig. 1, the particle size of the rare earth ore below 0.83mm accounted for 78.25%, indicating that the protolith had high weathered degree and the fine particles content of clay mineral was high, resulting in poor permeability of RE ore.

The clay mineral species and contents is a key factor to affect the permeability coefficients. The clay mineral was analysed by XRD which were separated from rare earth ore by natural sedimentation method according to Stokes' law (Li, 1982). The results were shown in Fig. 2.

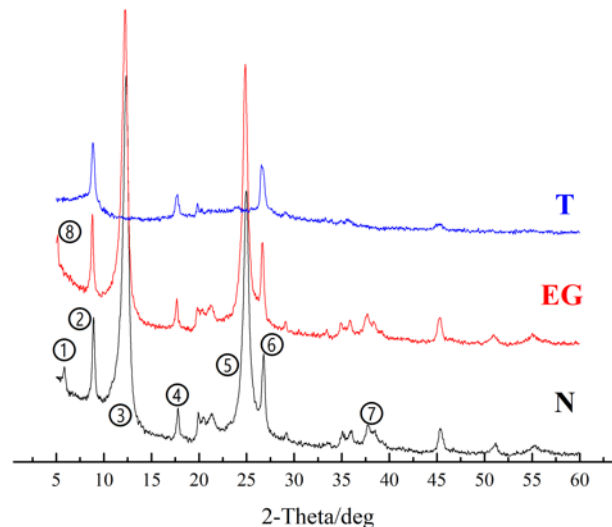


Fig. 2. XRD spectra of clay mineral - N: original sample, EG: Saturated sample with ethylene glycol, T: Sample was heated to 550°C for 2 hours

Because the characteristic peaks of kaolinite coincides with that of halloysite, the clay mineral samples was saturated with dimethyl sulfoxide to distinguish kaolinite and halloysite. And the results were shown in Fig. 3. In Fig. 2, peaks 3, 5, 7 were the characteristic peaks of kaolinite-group mineral which were disappeared after heating. Moreover, it can be seen from Fig. 3 that the intensity of peak 3 was decreased and a new peak appeared after sample was saturated with dimethyl sulfoxide, indicating that kaolinite-group mineral was composed of kaolinite and halloysite. Peaks 2, 4, 6 in Fig. 2 were the characteristic peaks of illite. Peak 1 in Fig. 2 was the characteristic peak of montmorillonite and was moved to peak 8 (Lin, 1988; Zhang and Fan, 2003). Therefore, the clay mineral species included kaolinite, halloysite, illite and montmorillonite.

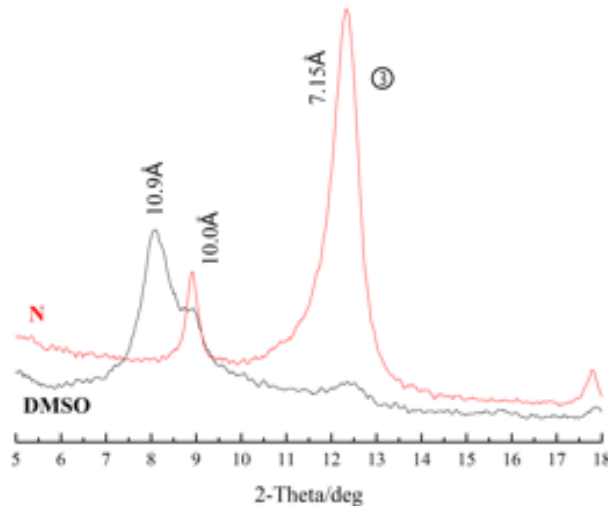


Fig. 3. XRD spectrums of saturated sample with dimethyl sulfoxide - DMSO: Saturated sample with dimethyl sulfoxide

The relative percentage content of each clay mineral could be calculated semi-quantitatively. The method of calculation was based on *SY/T 5163-2010* and kaolinite, halloysite, illite and montmorillonite were 9.88%, 78.45%, 10.64% and 1.03% respectively. Among them, montmorillonite has the biggest influence on permeability which results in easy hydration, expansion and dispersion. Therefore, clay minerals contain only a small amount of montmorillonite, which results in the permeability of rare earth minerals not too poor to make in situ leaching process feasible.

2.2. Methods

2.2.1. Experimental methods

The RE ore sample was dried in an oven at 353K for 8 hours, and then weighed 250g dried sample and poured into a glass column. First, add 1000ml ammonium carboxylate solution in advance to elute most of rare earth ions adsorbed in RE ore sample. After elution completed, adding ammonium carboxylate solution by a peristaltic pump to a certain height and keep it unchanged. Then collect leachate at regular intervals and measure the volume of leachate. The experimental device was shown in Fig. 4.

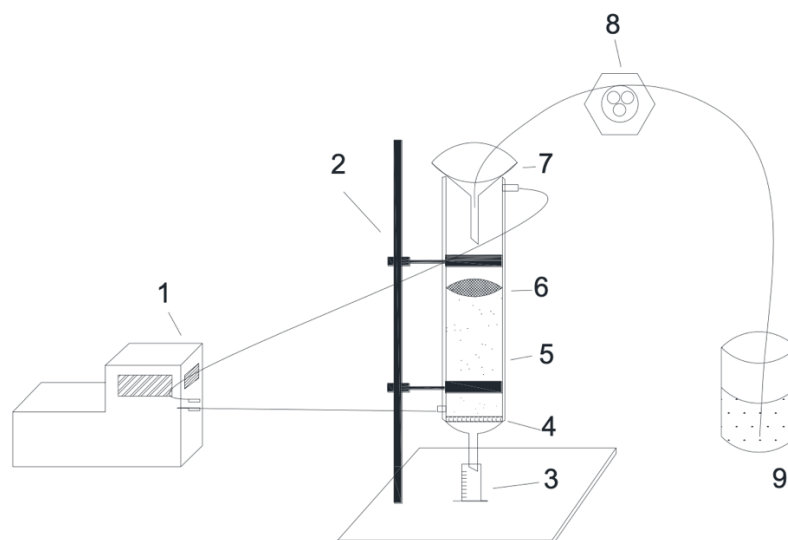


Fig. 4. Schematic diagram of experimental apparatus. 1-Thermostatic water tank, 2-Iron support, 3-Precision measuring cylinder, 4-Sand core filter plate, 5-Jacketed glass column, 6-filter paper, 7-Funnel, 8-Peristaltic pump, 9-Beaker

All the viscosities in this study were measured by PXWSN-265D ubbelohde viscometer from PingXuan Scientific Instrument Co., Ltd. (Shanghai, China). It's measuring scale of $0.6 \times 10^{-3} \sim 3 \times 10^{-3}$ Pa·s. The pH of ammonium acetate solution, ammonium tartrate solution and ammonium citrate solution were adjusted with ammonia and carboxylic acids of acetic, tartaric and citric, respectively. And the pH values of solutions were measured by the pH meter.

2.2.2. Analytical methods

The flow of liquid among ore particles will cause head loss because of liquid's viscosity. Darcy's law shows that seepage discharge is inversely proportional to hydraulic gradient and transverse area (formula 1). The equations are as follows (Wu et al., 2009):

$$Q = kAJ \quad (1)$$

$$v = \frac{Q}{A} = kJ = k \frac{h_w}{l} \quad (2)$$

$$k = \frac{\gamma}{32\mu} \cdot d_0^2 \cdot n \quad (3)$$

$$n = \frac{w_2 - w_1}{\rho} / V \quad (4)$$

In these formulas, Q is seepage discharge, cm^3/s ; k is permeability coefficient, cm/s ; A is transverse area, cm^2 ; J is hydraulic gradient, the mechanical energy loss of the unit length of permeation; v is seepage velocity, cm/s ; h_w is head loss, the mechanical energy loss of the unit mass of liquid during permeation, cm ; l is loading height, cm ; γ is liquid density, kN/m^3 ; μ is liquid's viscosity coefficient, $\text{pa}\cdot\text{s}$; d_0 is effective particle size, cm ; n is porosity, the ratio of the sum of all pore's space volumes in ore sample to the volume of the ore sample;

As for Formula (3), w_1 is mass of glass column containing dried sample, g ; Then adding water slowly until sample was saturated. w_2 is mass of glass column containing saturated sample, g ; ρ is water density, g/cm^3 ; V is volume of sample, cm^3 . Therefore, porosity of sample can be changed by changing the height of sample in glass column which leads V to be changed.

The k is used to represent the permeability of ores, which relates to the properties of fluid and ore. In Formula (3), the k is proportional to the bulk density (γ) of liquid and the quadratic of ore inter space size (d_0) and the porosity (n) of ore, inversely proportional to the viscosity coefficient (μ) of liquid (Bouffard and Dixon, 2001). Therefore, the larger the k , the better the permeability of ore. Obviously, the formula (2) is shown that the larger the permeability coefficient k , the larger the permeability velocity v is while the hydraulic gradient J is constant.

3. Results and discussions

3.1. Effects of concentration of leaching agent solution on permeability

The effects of concentration of ammonium carboxylate solution were investigated while the moisture of rare earth ores was zero and the porosity of rare earth ores was 0.50. Moreover, the temperature was 298k, and the results were shown in Fig. 5.

It can be seen from the Fig.5, the seepage velocities of leaching agent solutions in rare earth ores were increased linearly with the hydraulic gradients increased, which indicated that the seepage of ammonium carboxylate solution in rare earth ores followed Darcy's law. And the ammonium carboxylate solutions were in laminar flow state in the range of hydraulic gradients from 0.25 to 1.75 (Tian et al., 2001).

The slopes of the v - J line in Fig.5 are the permeability coefficients (k) (Tian et al., 2001). The slopes of the v - J line were calculated and the results were shown in table 2. As can be seen from Fig.5 and table 2, the permeability coefficients of ammonium acetate solution, ammonium tartrate solution and ammonium citrate solution with higher concentration ($c_{\text{am cit}} \geq 0.70\%$) were decreased with the concentration increased. The permeability coefficients of ammonium acetate solution were approximate to that of ammonium citrate solution while its concentration was higher than 0.70%. However, the poorest permeability coefficient was ammonium citrate solution with lower concentration ($c_{\text{am cit}} < 0.70\%$), followed by permeability coefficient of ammonium tartrate solution, which was the next poorest.

The permeability of ammonium carboxylate solution is determined by its physicochemical proper-

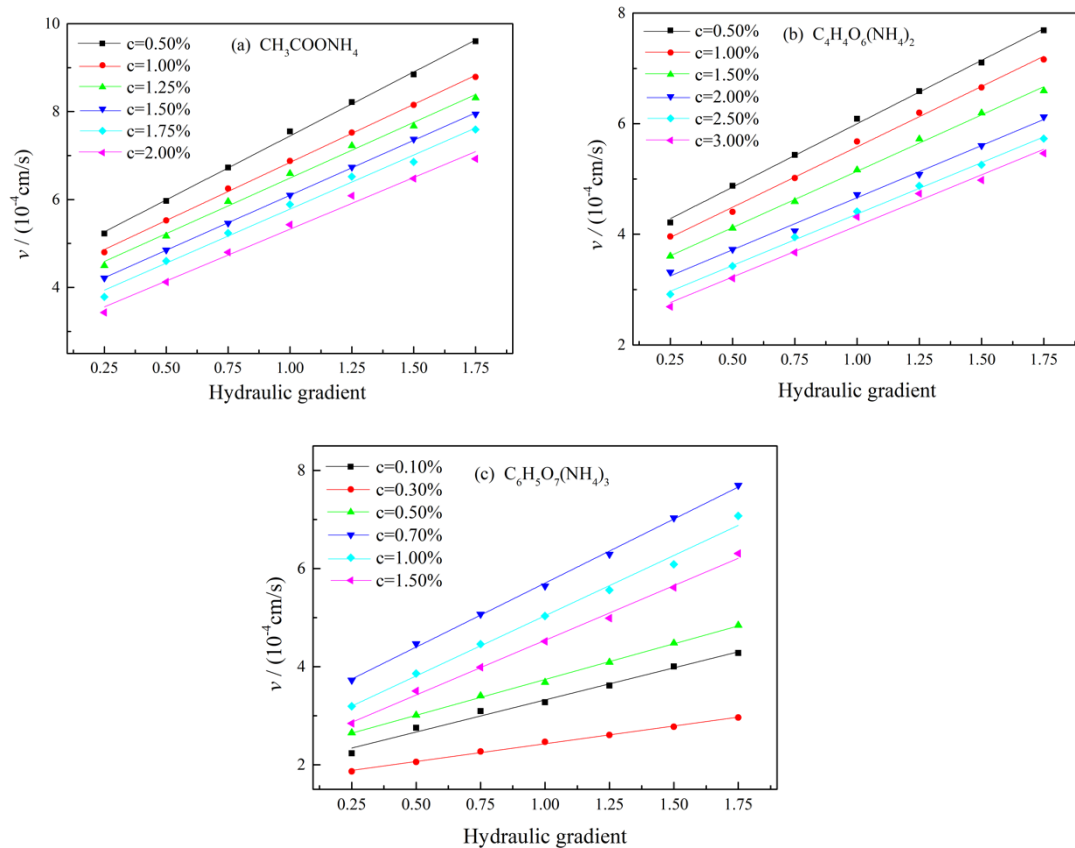


Fig. 5 Effects of concentration on the seepage velocity: (a) $\text{CH}_3\text{COONH}_4$, (b) $\text{C}_4\text{H}_4\text{O}_6(\text{NH}_4)_2$, (c) $\text{C}_6\text{H}_5\text{O}_7(\text{NH}_4)_3$

Table 2. The permeability coefficients (k) under different concentrations ($\times 10^{-4} \text{cm/s}$)

$c/(\text{g/mL})$	0.50%	1.00%	1.25%	1.50%	1.75%	2.00%
$k_{\text{am ace}}$	2.91	2.64	2.53	2.50	2.46	2.36
$c/(\text{g/mL})$	0.50%	1.00%	1.50%	2.00%	2.50%	3.00%
$k_{\text{am tar}}$	2.29	2.18	2.04	1.89	1.86	1.85
$c/(\text{g/mL})$	0.10%	0.30%	0.50%	0.70%	1.00%	1.50%
$k_{\text{am cit}}$	1.31	0.72	1.46	2.61	2.46	2.23

ties by Darcy's law, included viscosity and interaction between ammonium carboxylate and rare earth ores in the equal experimental conditions. According to the Formula (3), it is indicated that viscosity is inversely proportional to k , whereas the viscosity is linearly proportional to concentration. As shown in Fig. 6, the higher the concentration of leaching agent solution, the higher the viscosity. As a result, the permeability coefficient was decreased and the permeability of ammonium carboxylate solution was worse when the concentration was decreased.

However, the permeability coefficient of ammonium citrate solution changed at the concentration below 0.70%, which was related to the chemical properties of ammonium citrate itself. Compared with acetate anion and tartrate anion, citrate anion is easier to form complexes with rare earth cation (Li et al., 2015) and the forms of rare earth complexes would be varied with the concentration of ammonium citrate increased. Chen had found that the rare earth cation and citrate anion would be react and precipitate in the pH ranges from 6 to 8, while the concentration of ammonium citrate was below 0.30%. Then the permeability of rare earth ores would be decreased since the effective pores of rare earth ores

would be blocked up by precipitation. However, the rare earth cation and citrate anion would be reacted as $\text{RE}_2(\text{C}_6\text{H}_5\text{O}_7)_3^{3-}$ or $\text{RE}(\text{C}_6\text{H}_5\text{O}_7)_3^{2-}$, while the concentration was higher than 0.30% (Chen, 2013). Therefore, the permeability of rare earth ores would be increased until $c_{\text{am cit}} > 0.7\%$ because the precipitation dissolved. Meanwhile, the viscosity of ammonium citrate solution was also the key factor to affect the permeability of rare earth ores. After the precipitation was completely dissolved, the permeability of rare earth ores would be decreased since the viscosity of ammonium citrate solution increased while $c_{\text{am cit}} > 0.7\%$. Compared with ammonium citrate, the rare earth cation and tartrate anion would be reacted and precipitated in the concentration between 0.50% and 3.00% (Mei et al., 2001). Therefore, the permeability of rare earth ores in ammonium tartrate solution was lower than the other solutions except ammonium citrate solution with lower concentration ($c_{\text{am cit}} < 0.70\%$). Therefore, the permeability of ammonium citrate solution with $c_{\text{am cit}} = 0.7\%$ was the best. In order to ensure most of rare earth could be exchanged with NH_4^+ , $c_{\text{am ace}} = 1.00\%$, $c_{\text{am tar}} = 2.50\%$ and $c_{\text{am cit}} = 0.7\%$ were chose as experimental concentration.

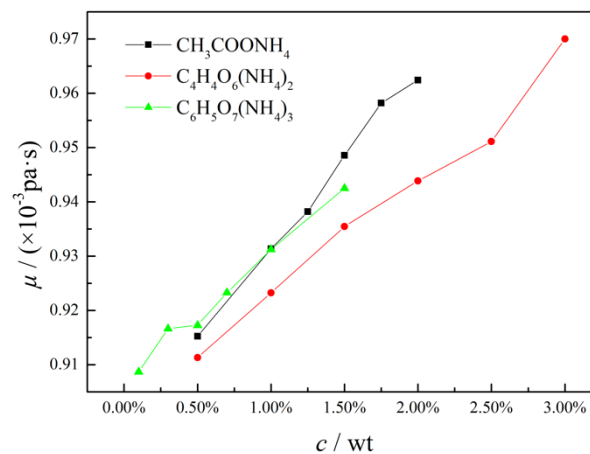


Fig. 6 Effects of concentrations on the viscosity of ammonium carboxylate solution

3.2. Effects of pH of leaching agent solution on permeability

The effects of pH of ammonium carboxylate solution were investigated while the moisture of rare earth ores was zero and the porosity of rare earth ores was 0.50. Moreover, considering the rare earth leaching rate, the concentrations of ammonium acetate solution, ammonium tartrate solution and ammonium citrate solution were 1.00%, 2.50% and 0.70% respectively, and the results were shown in Fig. 7. As it can be seen from the Fig. 7 that the seepage velocities of ammonium carboxylate solution in RE ores increased linearly with the increase of hydraulic gradients, which indicated that the seepage of amm-

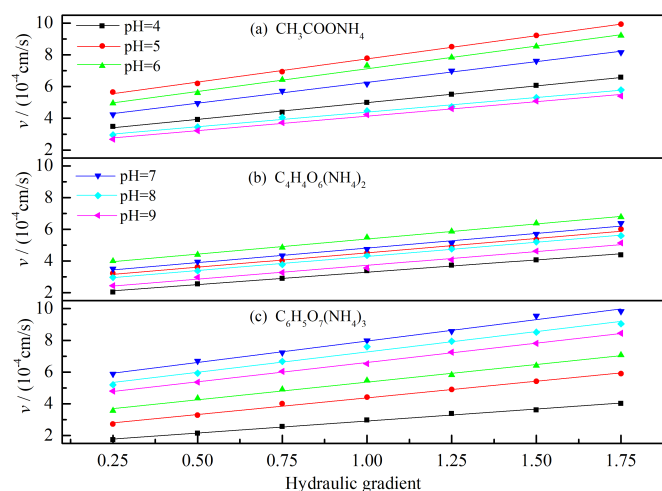


Fig. 7 Effects of different pH on the seepage velocity: (a) $\text{CH}_3\text{COONH}_4$, (b) $\text{C}_4\text{H}_4\text{O}_6(\text{NH}_4)_2$, (c) $\text{C}_6\text{H}_5\text{O}_7(\text{NH}_4)_3$

onium carboxylate solutions in RE ore samples followed Darcy's law. And the ammonium carboxylate solution was in laminar flow state in the range of hydraulic gradients from 0.25 to 1.75. The slopes of the v - J line obtained by Fig. 7 are the permeability coefficients (k), and the slopes of the v - J line were calculated and the results were shown in Table 3 is obtained as below.

Table 3. The permeability coefficients (k) in different pH ($\times 10^{-4}$ cm/s)

pH	4	5	6	7	8	9
$k_{\text{am ace}}$	2.11	2.92	2.86	2.62	1.84	1.83
$k_{\text{am tar}}$	1.56	1.82	1.91	1.85	1.80	1.75
$k_{\text{am cit}}$	1.51	2.10	2.22	2.70	2.57	2.44

As the Table 3 shown, the permeability coefficients of ammonium acetate, ammonium tartrate and ammonium citrate solution increased firstly and then decreased in the pH range from 4 to 9. Moreover, the maximum of permeability coefficients of ammonium acetate, ammonium tartrate and ammonium citrate solution were 2.92, 1.91 and 2.70, respectively, while the pH were 5, 6 and 7, respectively. It can be seen from table 4 that the effects of viscosity on ammonium carboxylate were not significant in the same concentration, where the pH were range from 4 to 9.

Table 4. Effects of pH on the viscosity (μ) of ammonium carboxylate solution ($\times 10^{-3}$ Pa·s)

pH	4	5	6	7	8	9
$\mu_{\text{am ace}}$	0.9667	0.9360	0.9330	0.9339	0.9338	0.9320
$\mu_{\text{am tar}}$	0.9229	0.9183	0.9176	0.9173	0.9180	0.9172
$\mu_{\text{am cit}}$	0.9685	0.9592	0.9539	0.9525	0.9526	0.9557

The surface electrical properties of clay minerals and the dissociation of ammonium carboxylate were notably affected by the pH of ammonium carboxylate solution. The main reasons could be included the following. Firstly, the carboxylate anions were adsorbed on the surface of clay minerals since the ammonium acetate, ammonium tartrate and ammonium citrate could be seen as surfactants. The solid-liquid interfacial tension and seepage resistance of boundary layer fluid flow could be decreased while the surfactants were added (Zhao et al., 2014). Secondly, there are amounts of fine clay minerals migrating and gathering at the bottom of rare earth ores due to the seepage of ammonium carboxylate solution. Then the effective interspaces were blocked, which lead the permeability of rare earth ores worse (Luo et al., 2014). Therefore, the migration of clay minerals in rare earth ores was inhibited by adding the surfactants (Liu et al., 2014).

The permeability was mainly depended on the ammonium carboxylate anion absorbed on the surface of clay minerals, whereas the adsorption process was depended on the pH of ammonium carboxylate solution. Moreover, the adsorption capacity of ammonium carboxylate anion on the surface of rare earth ore is strongest while the pH of ammonium carboxylate solution is close to its pK_a . The pK_a of ammonium acetate and ammonium citrate were shown in the Table 5.

Table 5. Comparisons between pK_a (Dean, 2003) of ammonium acetate and ammonium citrate and optimum pH

Leaching agents	Ammonium acetate	Ammonium citrate
Optimum pH	5	7
pK_a	$\text{pK}_a = 4.76$	$\text{pK}_{a1} = 3.13$ $\text{pK}_{a2} = 4.76$ $\text{pK}_{a3} = 6.40$

The reason was that the water molecule could be seen as proton acceptor and proton donor, then ammonium carboxylate anion could be protonated and the hydroxyl on clay mineral surface in the solution of ammonium carboxylate could be deprotonate. However, the possibility of protonation and deprotonation could be decreased while the pH of ammonium carboxylate solution is close to its pK_a ,

since the capacity of water molecule to adsorb competitively proton was close to the ammonium carboxylate anion and hydroxyl on clay mineral surface. Then the capacity to form hydrogen bond between hydroxyl on clay mineral surface and ammonium carboxylate anion was increased (Chen, 2014). As results, the amount of ammonium carboxylate anion absorbed on clay minerals surface was increased. Therefore, the permeability of ammonium acetate and ammonium citrate solution was the best while the pH were close to its pK_a . However, the ammonium tartrate would be dissociated to $C_4H_5O_6^-$ and $C_4H_4O_6^{2-}$ that could form stable complexes with metal ions, especially, as coordination ions, the $C_4H_5O_6^-$ and $C_4H_4O_6^{2-}$ could react with Al^{3+} to form insoluble and stable complex that blocked effective pore in pH from 3 to 6 (Fang et al., 2018). Therefore, the permeability of ammonium tartrate solution was worse than the ammonium acetate and ammonium citrat.

3.3 Effects of temperature of leaching agent solution on permeability

The effects of temperature of ammonium carboxylate solution were investigated while the moisture of rare earth ores was zero and the porosity of rare earth ores was 0.50. Moreover, the concentrations of ammonium acetate, ammonium tartrate and ammonium citrate were 1.00%, 2.50% and 0.70%, respectively, and the results were shown in Fig. 8.

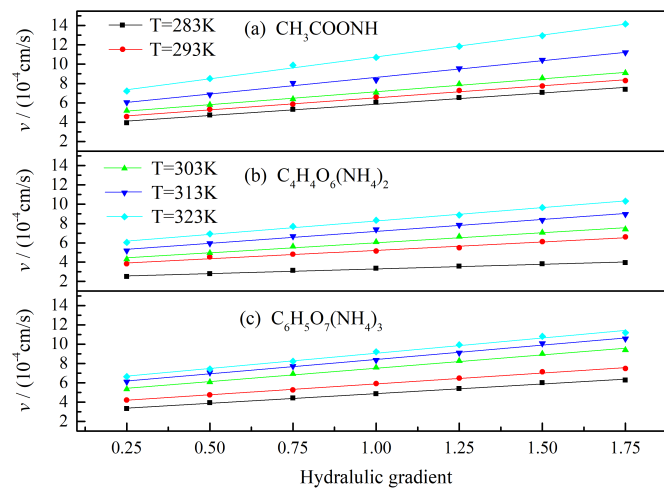


Fig. 8 Effects of temperature on the seepage velocity: (a) CH_3COONH_4 , (b) $C_4H_4O_6(NH_4)_2$, (c) $C_6H_5O_7(NH_4)_3$

It can be seen from the Fig.8 that the seepage velocities of ammonium carboxylate solutions in rare earth ores were increased linearly with the hydraulic gradients increased, which indicated that the seepage of ammonium carboxylate solutions in rare earth ores followed Darcy's law. And the ammonium carboxylate solutions were in laminar flow state in the range of hydraulic gradients from 0.25 to 1.75. The slopes of the v - J line calculated from Fig.8 are the permeability coefficients (k). The slopes of the v - J line were shown in Table 6.

Table 6. the permeability coefficients (k) at different temperatures ($\times 10^{-4}cm/s$)

T/K	283	293	303	313	323
$k_{am\ ace}$	2.33	2.50	2.67	3.45	4.53
$k_{am\ tar}$	0.97	1.75	2.08	2.47	2.78
$k_{am\ cit}$	2.00	2.25	2.76	2.97	3.15

It can be seen from table 6 that the permeability coefficients were increased significantly with the temperature of ammonium carboxylate solutions increased. it can be concluded from table 6 that the permeability coefficients of different ammonium carboxylate solutions were followed the orders: $k_{am\ ace} > k_{am\ cit} > k_{am\ tar}$ in the same temperature. The permeability coefficients of solutions were affected by viscosity and skeleton structure of clay mineral particles. The effects of temperature on the viscosity of ammonium carboxylate solution were shown in Fig. 9.

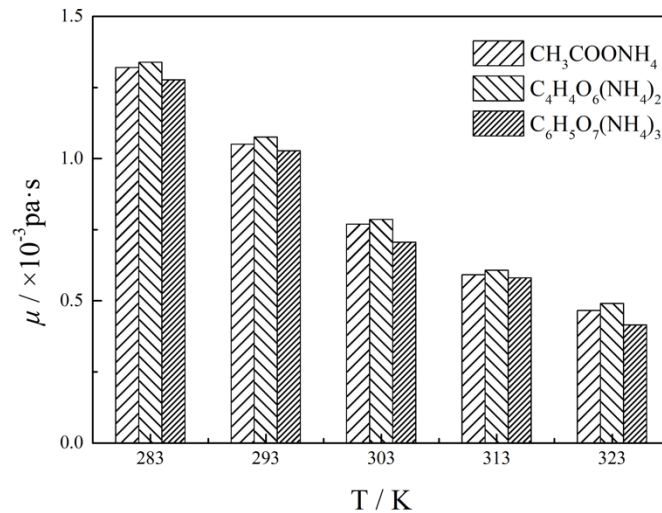


Fig. 9 Effects of temperature on the viscosity of ammonium carboxylate solution

It could be seen from Fig. 9 that the viscosity of ammonium carboxylate solution was decreased with the temperature of solutions increased. According to the Formula (3), it is indicated that viscosity of leaching agent solution is inversely proportional to permeability coefficient. As results, the permeability coefficient was increased with the temperature of ammonium carboxylate solution increased. Moreover, the micro skeleton structure of clay minerals particles was affected by the temperature of ammonium carboxylate solutions. Under the effect of solution seepage pressure with the temperature changed, some clay minerals particles were easily to decompose and dissolve with the temperature of carboxylate solutions increased. Then there were more new seepage channels and more effective pore would be formed in rare earth ore (Poisson et al., 2009; Mcdowell-Boyer et al., 2016). As results, the permeability of rare earth ores was improved.

3.4 Effects of particle size and porosity on permeability

The effect of particle size and porosity of rare earth ore were investigated while the moisture of rare earth ores was zero and the concentrations of ammonium acetate, ammonium tartrate and ammonium citrate were 1.00%, 2.50% and 0.70%, respectively. The results were shown in Fig. 10. It can be seen from the Fig.10 that the seepage velocities of ammonium carboxylate solutions in rare earth ores increase linearly with the hydraulic gradients increased, which indicated that the seepage of ammonium carboxylate solutions in rare earth ores followed Darcy's law. And the ammonium carboxylate solutions were in laminar flow state in the range of hydraulic gradients from 0.25 to 1.75. The slopes of the v - J line calculated from Fig.10 are the permeability coefficients (k). The slopes of the v - J line were shown in Table 7.

The permeability of rare earth ores was determined on the structure and the pores characteristic of clay minerals (Qiu et al., 2004). Therefore, the permeability was affected by particle size and porosity of rare earth ore. According to the table 7, the permeability coefficients of rare earth ore were decreased with the particle size decreased while the porosities of rare earth ores were approximate. For example, there are four particle size fractions in table 7, included $-0.83\sim+0.25$ mm, $-0.25\sim+0.15$ mm, $-0.15\sim+0.109$ mm and -0.109 mm, while the porosities was approximate to 0.505. And the permeability coefficients of rare earth ores were followed the order: $-0.83\sim+0.25$ mm $>$ $-0.25\sim+0.15$ mm $>$ $-0.15\sim+0.109$ mm $>$ -0.109 mm. It was demonstrated that permeability coefficients were decreased with the particle size of rare earth ores decreased since the larger particles in rare earth ores were easily form skeletons benefited the seepage of solutions (Qiu et al., 2004). Moreover, the smaller particles of rare earth ore have larger specific surface area under the same volume. Therefore, the leaching agent solution needs to bypass more ore particles and flows longer distance which enhances the viscous effect and the permeability of rare earth ore get worse (Li, 2016).

It can also be seen from table 7 that the larger the porosity of rare earth ore is, the larger the permeability coefficient is in the equal particle size. The reason was that the larger the porosity of rare earth ore, the more leaching agent solution could pass per unit time (Shepherd, 1989). Therefore, the permeability of rare earth ore was increased.

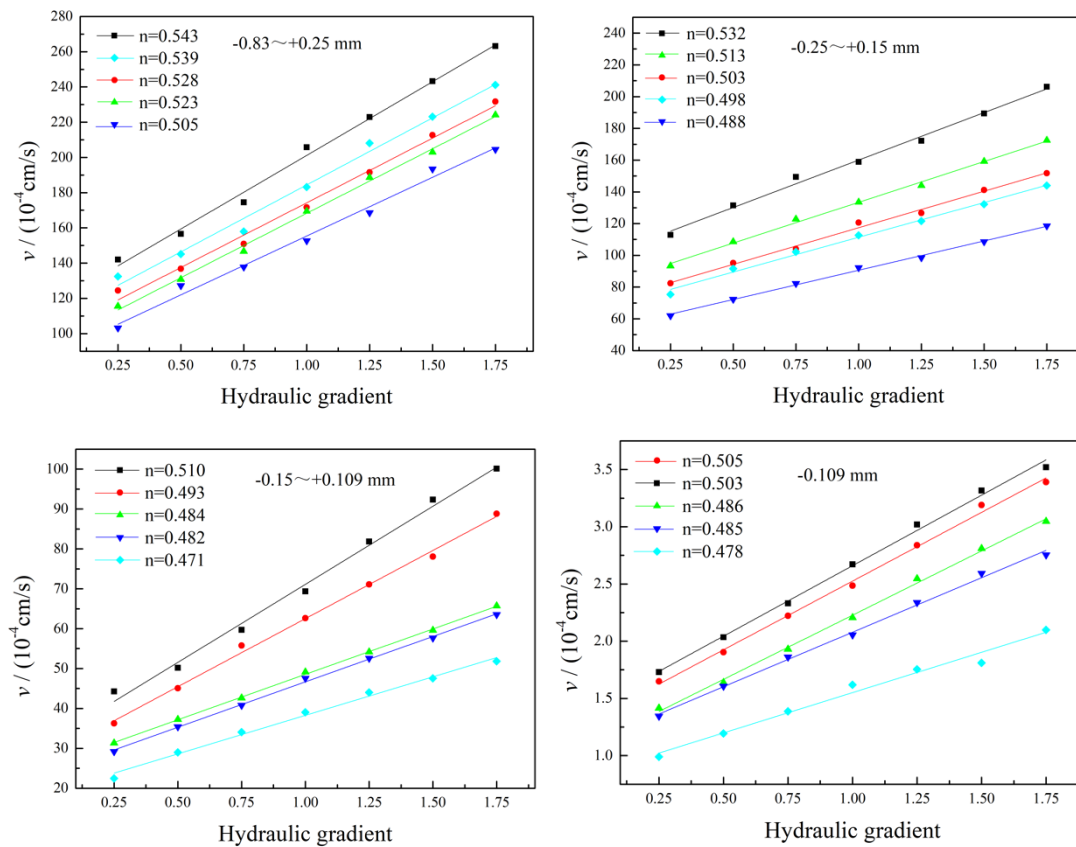


Fig. 10 Effects of different porosity on the seepage velocity in different size fraction: (a) -0.109 mm, (b) -0.15~+0.109 mm, (c) -0.25~+0.15 mm, (d) -0.83~+0.25 mm

Table 7. the permeability coefficients (k) in different porosities of different size fractions ($\times 10^{-4}$ cm/s)

Particle size / mm	porosity	0.543	0.539	0.528	0.523	0.505
-0.83~+0.25	k	83.61	76.15	73.53	73.22	66.71
	porosity	0.532	0.513	0.503	0.498	0.488
-0.25~+0.15	k	59.88	51.40	46.14	43.81	36.93
	porosity	0.510	0.493	0.484	0.482	0.471
-0.15~+0.109	k	39.15	34.21	22.86	22.87	19.34
	porosity	0.505	0.503	0.486	0.485	0.478
-0.109	k	1.23	1.20	1.12	0.96	0.70

4. Conclusions

In this paper, the effects of concentration, pH, temperature, particle size and porosity on the permeability were studied. The results shown that the seepage velocity of ammonium carboxylate solution was increased with hydraulic gradient increased, and shown a linear relationship in the range of above experimental conditions which indicates that the seepage of ammonium carboxylate solution in rare earth ore follows Darcy's law and the ammonium carboxylate solution is in laminar flow state in the studied hydraulic gradient. The permeability coefficients are inversely proportional to concentrations of ammonium acetate, ammonium tartrate and ammonium citrate whose concentration is greater than 0.7wt%, because the insoluble complexes formed by the reaction of ammonium citrate with RE^{3+} at lower concentration decrease the permeability coefficient. To ensure leaching rate of rare

earth, the used concentrations of ammonium acetate, ammonium tartrate and ammonium citrate are 1.00%, 2.50%, 0.70% respectively. All three kinds of ammonium carboxylate solutions' permeability coefficients increase firstly and then decrease with the pH increased. The maximum of permeability coefficients of ammonium acetate, ammonium tartrate and ammonium citrate solution were 2.92×10^{-4} cm/s, 1.91×10^{-4} cm/s and 2.70×10^{-4} cm/s, respectively, while the pH of solution were 5, 6 and 7, respectively. Increasing temperature is beneficial for the seepage of ammonium carboxylate solution in orebody, therefore, it is helpful for leaching operation in summer. Moreover, clay minerals particle size and porosity are the key factors affecting the permeability of ammonium carboxylate solution in orebody.

The permeability coefficients of ammonium acetate, ammonium tartrate and ammonium citrate solutions are 2.92×10^{-4} cm/s, 1.90×10^{-4} cm/s and 2.69×10^{-4} cm/s, respectively, at the same temperature of 293K, original particle size and porosity of the ore. In the case of the concentration of leaching agent is sufficient to elute most of rare earth, the improvement of permeability is a vital technological approach to increase leaching efficiency of rare earth and shorten the period of leaching process. Moreover, the ore slope and collection system would be stabilized. Ammonium acetate solution has the best permeability in orebody. To ensure leaching rate of rare earth, 1.00wt.% ammonium acetate solution was chosen as leaching agent solution of weathered crust elution-deposited rare earth ores.

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