

Correlation Evaluation of Ion Adsorption-Based Rare Earth Leaching Performance Based on Zeta Potential Drop Leaching

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Abstract

Rare earth elements are indispensable raw materials for advanced aero-engines, special optical materials, and high-performance electronic products. With the development of the social economy, the global demand for rare earth resources is increasing, and rare earths have become a key metal for the development of new industries and frontier technologies that are highly valued both at home and abroad. Ion-adsorbed rare earth ores are an important source of rare earths, so the efficient green leaching of ion-adsorbed rare earths is important. Researchers found that the selection of an efficient green leaching agent for ion-adsorbed rare earths is based on the zeta potential of tailing clay minerals in addition to leaching efficiency, and both zeta potential and leaching ion concentration are related to mineral acidity and alkalinity, and the pH of tailing water suspension is a direct indicator of environmental water quality requirements. Therefore, the efficiency of the leaching process is closely integrated with the environmental evaluation, and the characteristics and correlation of the changes in zeta potential, pH, conductivity and pollutant concentration of the pulp of clay mineral content during the leaching process of ore leaching and tailings aqueous electrolyte solution leaching are studied by evaluating the leaching system, and a set of correlation leaching efficiency and environmental impact evaluation method is established based on the results of the above analysis, which is of scientific development of ion adsorption rare earth resources. It has important theoretical significance and practical application value.

Keywords

Ion Adsorption Rare Earth, Ph Value, Zeta Potential, the Leaching Efficiency

1. Introduction

The leaching efficiency of ion adsorption type rare earths is usually leached by 2 wt% ammonium sulfate solutions with 100% rare earth content by full drenching, and the amount of rare earths leached by other leaching agents compared to it, which is the leaching efficiency [1]. The leaching efficiency is affected by the type of leaching agent, concentration, pH, leaching method, type of ore sample, solid-liquid ratio, etc. As far as leaching agents are concerned, different types of leaching agents leach different efficiencies under the same conditions. Sun Yuan-yuan [2] reported that the leaching efficiencies of different electrolytes were different at a cation concentration of 0.128 mol/L. The leaching efficiencies were in the order of $(\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{Cl} > \text{K}_2\text{SO}_4 > \text{KNO}_3 > \text{KCl} > \text{Na}_2\text{SO}_4 > \text{NaCl} > \text{NaNO}_3$, and Yang Lifan [3] reported that at an equivalent concentration of 0.128 N, the leaching efficiencies of the following leaching agents in the following order: $\text{Al}_2(\text{SO}_4)_3 > (\text{NH}_4)_2\text{SO}_4 > \text{AlCl}_3 > \text{Al}(\text{NO}_3)_3 > \text{NH}_4\text{NO}_3 > \text{NH}_4\text{Cl} > \text{MgSO}_4 > \text{Mg}(\text{NO}_3)_2 > \text{CaCl}_2 > \text{Ca}(\text{NO}_3)_2 > \text{MgCl}_2$, and Xiao Yanfei [4] *et al.* reported that at a leaching agent concentration of 0.1 mol/L pH = 2, the leaching efficiency of $\text{Fe}_2(\text{SO}_4)_3 > \text{FeSO}_4 > \text{MgSO}_4 > \text{ZnSO}_4 > \text{Fe}(\text{NO}_3)_2 > \text{FeCl}_2 > \text{MnSO}_4 > \text{Mg}(\text{NO}_3)_2 > \text{MgCl}_2 > \text{K}_2\text{SO}_4 > (\text{NH}_4)_2\text{SO}_4$. It can be seen that the order of leaching efficiency is not the same when different treatments are adopted. Different concentrations of the same leaching agent leaching effect also vary, generally speaking, the greater the concentration of the leaching agent, the higher the leaching efficiency, but the high concentration of magnesium sulfate (5 wt%) leaching effect is better than the same concentration of ammonium sulfate, while aluminum sulfate at a lower concentration has a good leaching efficiency. The leaching method also has an impact on the leaching effect, the current common leaching methods are: static leaching, heap leaching, balanced leaching, and column drenching. The leaching efficiency is generally: column drenching > equilibrium leaching > static leaching. This is due to the on-column drenching, leaching agent solution under the action of its own gravity, and top-down contact with the solid phase several times for ion exchange, the process is a dynamic equilibrium, exchange after the separation of products, exchange more fully. On-column drenching usually uses a sample volume ranging from a few tens of grams to several kilograms, depending on the size of the filled column. On-column drenching is influenced by the degree of filling uniformity, the granularity of the mineral sample, the degree of filling compaction, the height of the filled column, etc. The degree of filling uniformity determines whether the leaching agent has gully flow, bias flow, etc., thus making some ore samples over-leached and some unleached. Tian Jun [5] *et al.* reported that the ore particle size has a great influence on the leaching rate and the leaching rate of rare earths decreases with the increase of particle size. Large granularity has more pores, fast leaching agent flow rate, and insufficient leaching agent exchange; small granularity, sufficient leaching agent exchange, but slow flow rate, the existence of re-adsorption phenomenon, and serious tail dragging. The loading column height is similar to the column efficiency theory of chromatographic column, the column height deter-

mines the theoretical tower plate number, *i.e.*, the number of cycles of adsorption-desorption, but the column drenching is significantly different from the larger the column height of chromatographic column when the injection volume is certain. When the solid-liquid ratio is fixed, the effective exchange of solutions is limited, and the first part of the solution can effectively participate in the exchange, after the solution exchange is limited, and the increase of the filling column is limited. The compaction of the filling and the particle size of the sample affect the height and porosity of the filling column, thus affecting the flow rate or the height of the leaching peak and the sequence of the peak time [6]-[10]. Equilibrium leaching uses equilibrium oscillation to exchange to reach equilibrium and is usually used to study the thermodynamic model of ion-adsorption rare earths, adsorption model, etc. The amount of ore samples used is within a few tens of grams, and most of them are screened clay minerals, and the control of ore sample type, temperature, leaching time, etc. is simple and easy to study. The equilibrium leaching method to study the efficiency of leaching needs to be further standardized.

In this paper, potentiometric titration is used to study the leaching performance of ion-adsorbed rare earths, which is different from the common oscillatory equilibrium leaching. Unlike acid-base potentiometric titration which has obvious mutation points, the potentiometric titration of a leaching agent has no obvious mutation points except the initial point and the appearance of the color remains unchanged, so it is impossible to judge the end point of titration directly. The change of Zeta potential reflects the change of internal charge of clay minerals slip surface, which is the result of the joint action of anion and cation. The clay minerals generally have a negative skeleton charge, when the clay minerals adsorb more cations, the more negative charges are offset, and the negative value of Zeta potential decreases. When the rare earth content changes, there must be ions involved in the exchange, and the zeta potential generally changes [11] [12]. For this reason, by determining the content and concentration of the leaching agent added drop by drop and the leaching amount of rare earth ions, the correspondence will be able to evaluate the leaching performance of the leaching agent at different concentrations. In addition to the determination of the rare earth content, the ion-adsorbed rare earth minerals were titrated by potentiometric dip leaching to monitor the changes in zeta potential, pH and conductivity during the leaching process and to provide a basis for the interpretation of the ion exchange process.

2. Experimental part

2.1. Apparatus and Reagents

1) Main experimental apparatus

Name of instrument	Manufacturers
UPT-I-10T ultrapure water device Sichuan	UPT Ultrapure Technology Co.

Continued

A80045-Zeta Probe	Colloidal Dynamics
DKZ-2 water bath constant temperature oscillator	Shanghai Jinghong Instrument and Equipment Co.
Electric Heating Constant Temperature Blast Dryer	Shanghai Jinghong Instrument Equipment Co.
AG-135 Electronic Balance	Sartorius Scientific Instruments Co.
Bettersize 2000LD	Dandong Baite Instrument Co.
PHS-25 acidity meter	Shanghai Yifen Scientific Instruments Co.

2) Main experimental reagents

Reagents	Purity	Manufacturer
Ammonium sulfate	Analytical purity (AR)	Xilong Chemical Co.
Magnesium sulfate	Analytical purity (AR)	Xilong Chemical Co.
Aluminum sulfate	Analytical purity (AR)	Tianjin Damao Chemical Reagent Factory
Ammonium chloride	Analytical purity (AR)	Xilong Chemical Co.
Magnesium chloride	Analytical purity (AR)	Sinopharm Group Chemical Reagent Co.
Aluminum Chloride	Analytical pure (AR)	Tianjin Damao Chemical Reagent Factory
Glacial acetic acid	Analytical pure (AR)	Xilong Chemical Co.
Ammonium acetate	Analytical pure (AR)	Xilong Chemical Co.
Arsenic azo-III	Analytical pure (AR)	West Asia Chemical Technology Co.

2.2. Experimental Steps**2.2.1. Determination of Abrasion pH, Exchange pH, and On-Column Drenching pH**

Abrasion pH: Take 20.00 g of the screened mineral sample below 20 mesh and deionized water mixed in the ratio of 1:4 by mass, put it in a 250 ml beaker, put it on a multi-head magnetic stirrer and stir for 30 min, set the speed to 1000 r/s, and then filtered, take the clarified filtrate, and determine its pH value as the abrasion pH value.

Exchange pH value: take 20.00 g of screened ore sample below 20 mesh and 2 wt% ammonium sulfate mixed according to mass ratio 1:4, put it in 250 ml beaker, put it on a multi-head magnetic stirrer and stir, set the speed to 1000 r/s, stirred for 30 min, then filtered, take the clarified filtrate, measure its pH value is the exchange pH value with 2 wt% ammonium sulfate. The exchange pH of different mineral samples and different components of the same mineral sample with different types and concentrations of leaching agents are different.

Leaching pH on the column: 300 g of ore samples below 20 mesh were uniformly packed into a $\Phi \times H = 60 \text{ mm} \times 400 \text{ mm}$ sand-core quartz column and 300 ml of 2 wt% $(\text{NH}_4)_2\text{SO}_4$ solution was added at a solid-liquid ratio of 1:1. Each 10 ml of leachate was collected and the pH value of each leachate was measured. Experimental plots are shown in **Figure 1**.

2.2.2. Zeta Potential Drip Leaching Ion Adsorption Type Rare Earth Ore

The clay samples were accurately weighed and mixed with 250 ml of deionized water, equilibrated in a constant temperature shaker at 25°C for 30 min, and the Zeta potential during the leaching process was measured on an A80045-Zeta Probe at an adjusted speed of 200 rpm, using a certain concentration of leaching agent added drop by drop to the samples, and the Zeta potential, pH and conductivity were measured every 0.5 ml. The Zeta potential, pH and conductivity were measured every 0.5 ml, and for every 2 ml of leaching agent, 2 ml of sample was taken to determine the rare earth content, where the amount of leaching agent added drop by drop and the volume change were known, and the leaching agent concentration corresponding to the recorded data could be clearly calculated. When the drip addition of the leaching agent was stopped, the tailings were filtered and leached with 250 ml of deionized water to determine their zeta potential during water leaching. During the determination of Zeta potential, the corresponding leaching and water leaching pH values were measured, and the equilibrium leaching filtrate pH was determined.

3. Results and Discussion

3.1. Evaluation of the Integrated Correlation between Zeta Potential and Leaching Performance

Abrasion pH measures the pH of clay minerals in pure water, which reflects the

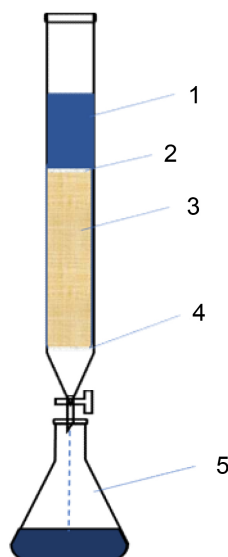


Figure 1. Experimental leaching device diagram 1- Leaching solution, 2- Quantitative filter paper, 3- Ion adsorption type rare earth ore, 4- Quartz cartridge, 5- Conical Bottle.

hydration characteristics of the clay particles. The clay particles are negatively charged, and the cations inside the slip surface can only partially counteract the negative charge, and cations that maintain electrical neutrality will be present in the diffuse layer of the clay minerals. In pure water, the whole clay minerals resemble the hydrolysis of strong acid and weak base salts, the cations in the diffusion layer enter the solution, and the overall equivalent of a negatively charged group inside the slip surface, the group can combine with H^+ in the water, and the OH^- in the solution increases, making the abrasion pH generally larger. Exchange pH measures the pH of clay minerals in the leaching and exchange process. The change of exchange pH is influenced by the hydration of ions and groups in the exchange process but is mainly determined by the anion and cation of the leaching agent.

Table 1. Abrasion pH and exchange pH of Longnan, Anyuan and Dingnan ore samples.

Sample No.	Longnan abrasion pH	Lonan exchange pH	Anyuan abrasion pH	Anyuan exchange pH	Dinan abrasion pH	Dinan exchange pH
1	5.47	4.34	6.13	4.3	5.7	4.5
2	5.35	4.33	6.14	4.32	6.18	4.49
3	5.5	4.33	6.18	4.28	5.76	4.48
4	5.74	4.39	5.92	4.43	5.72	4.72
5	5.67	4.39	5.93	4.39	5.69	4.75
6	5.68	4.43	6.24	4.37	5.71	4.74
Average	5.57 ± 0.13	4.37 ± 0.03	6.09 ± 0.11	4.35 ± 0.05	5.80 ± 0.13	4.61 ± 0.12

From **Figure 2**, the abrasion pH and exchange pH of the mine samples from Longnan, Anyuan and Dingnan can be seen that the abrasion pH of the mine samples from all three regions is higher than the exchange pH, which is due to the combination of negatively charged clay particles with H^+ in water, which makes the solution OH^- increase and the abrasion pH rise. The higher the abrasion pH, the stronger the hydration process of clay minerals, the more sparse the structure of the original ore in aqueous solution, and the more likely to cause soil erosion, and the loss of fine particles makes the surviving ore bodies generally exist in the form of biased large particles, which is consistent with the large granularity and less fine particles in An Yun area. The larger pH value of Dingnan exchange is due to the fact that the same ore sample with less than 20 mesh, There are more fine particles of clay distribution in the Dingnan ore sample, and the clay mineral skeleton is negatively charged and easy to combine with H^+ . Under the same conditions of leaching agent solution, there are more fine particles of clay distribution and more combined H^+ , thus the exchange pH value of Dingnan is larger.

From **Figure 2**, the column-drenching pH values of the Longnan, Anyuan and Dingnan ore samples show that the column-drenching pH values of the ore

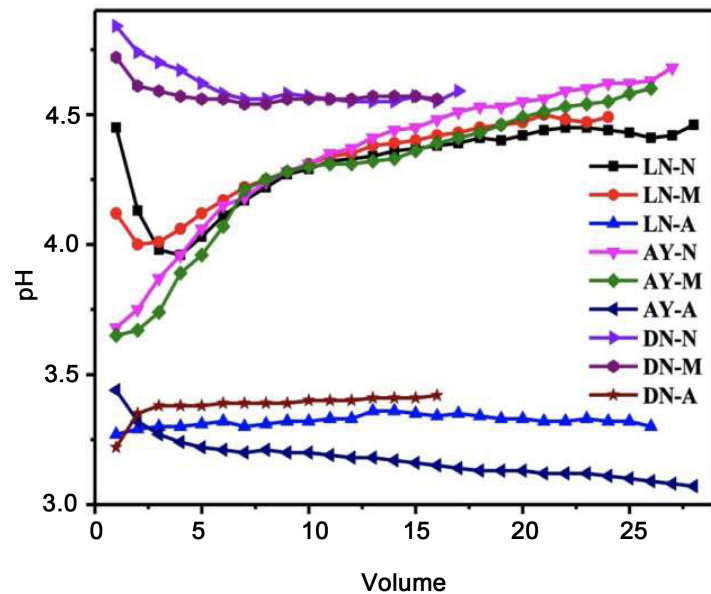


Figure 2. Leaching pH values on the columns of Longnan, Anyuan and Dingnan ore samples.

samples from the three regions and the three leaching agents show different patterns. The pH of leaching with ammonium sulfate and magnesium sulfate was higher and showed a trend of decreasing and then stabilizing finally at pH = 4.5. The higher pH of Dingnan ore sample was due to the fact that Dingnan ore sample contained the most fine particles of clay among 300 g of ore samples below 20 mesh, and the clay mineral skeleton was negatively charged and easily combined with H^+ . The pH value of the exchange is larger; the pH value of the Anyuan mine sample leaching with ammonium sulfate and magnesium sulfate has been on a rising trend, which is due to the strong hydration ability of the Anyuan mine sample, the clay particles have been adsorbing H^+ and the pH value has increased; the pH value of Lonnan mine sample leaching with ammonium sulfate and magnesium sulfate shows a falling trend first and then rising trend, and its rising trend is slightly lower than that of Anyuan mine sample, where the pH value falls first because H^+ is first was exchanged out first, and then the hydration process of the mineral sample was strengthened, and the clay particles kept adsorbing H^+ and the pH value increased. Comparing the pH of drenching on the column of ammonium sulfate with the pH of equilibrium leaching, Dinan (4.61) > Longnan (4.37) > Anyuan (4.35), it can be seen that the pH of drenching on the column and the pH of equilibrium leaching are generally the same. The difference is that equilibrium leaching is a single equilibrium showing the final result of the exchange, while column drenching is multiple dynamic equilibria, which can reflect the changes of the whole exchange process on the column.

3.2. Evaluation of Integrated Correlation between Zeta Potential and Leaching Performance

The pH of mineral samples can be usually divided into two categories: abrasion

pH and exchange pH. abrasion pH is the solution pH of mineral samples in deionized water, which is the result of the overall charge balance of clay minerals, dissociation equilibrium and the formation of hydrogen bonds at the local fracture surface together with water, exchange pH is the solution pH measured after the exchange of mineral samples with leaching agent, which is closely related to the type and concentration of leaching agent, usually referred to as exchange pH. The pH of the exchange of minerals with 2 wt% ammonium sulfate, low exchange pH indicates that more cations inside the slip surface of clay minerals enter the solution to combine with OH^- or the overall negative charge inside the slip surface of clay minerals decreases due to the decrease of H^+ involved in charge balance and the increase of free H^+ . The change in solution pH indicates that H^+ and OH^- are involved in ion exchange between clay minerals and leaching agents, and the equilibrium of H^+ and OH^- in the solution has been stabilized with constant solution pH. The relationship between leaching agent concentration and pH change during potentiometric drip leaching in **Figure 3** shows that the pH change of Anyuan ore sample decreased slightly with 0.15 mol/L MgSO_4 leaching agent drip, while the pH of Longnan ore sample decreased sharply and then decreased slowly, and the pH of Dingnan ore sample decreased sharply and then increased slightly, the exchange pH of Longnan ore sample was around 4.6 - 4.9, and the exchange pH of Dingnan ore sample was around 4.5 - 4.7, which was different from the starting pH.

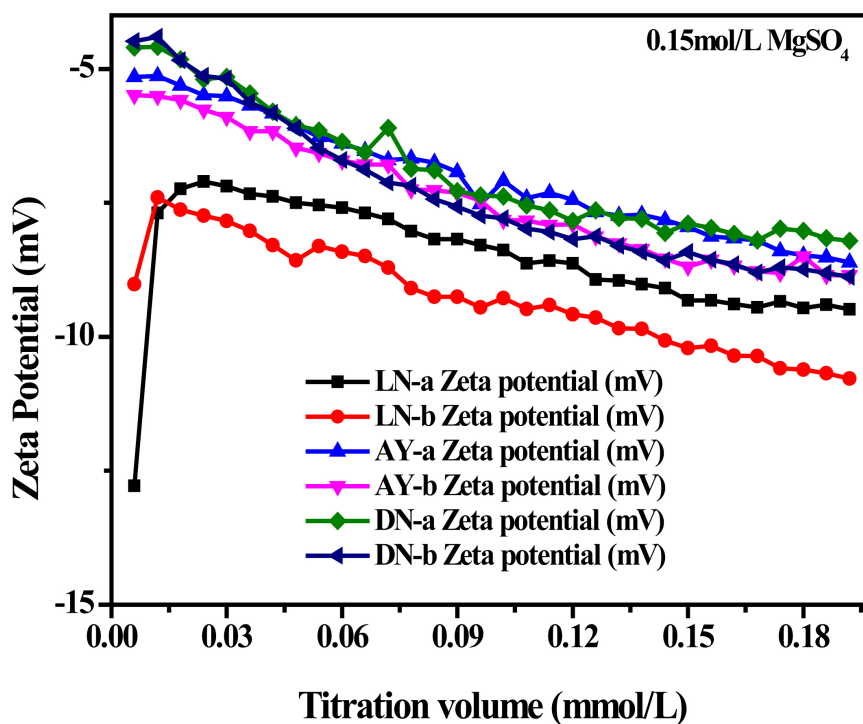


Figure 3. Variation of leaching agent concentration versus zeta potential.

The zeta potential of the ore sample is the clay mineral slip surface potential, and the change of zeta potential can reflect the charge change of the internal structure of the clay mineral slip surface, so as to infer the distribution of cation and anion during ion exchange of the internal structure of the clay mineral slip surface. The relationship between the concentration of the leaching agent and the change of zeta potential during a potentiometric dip is shown in **Figure 4**. With the addition of a leaching agent, the high-valence rare earth ions inside the slip surface were exchanged by Mg^{2+} , and the positive charge inside the slip surface decreased and the negative value of Zeta potential increased.

The conductivity of the solution of the mineral sample dispersion system reflects the change of charge in the solution, and the dispersed clay minerals are regarded as a whole agglomerate structure, and the solution conductivity changes gradually with the addition of electrolyte to the solution as the ions in the solution gradually increase. From **Figure 5**, the relationship between the concentration of the leaching agent and the change of conductivity can be seen, with 0.15 mol/L $MgSO_4$ leaching agent drop into the conductivity is a linear increasing trend, different mine samples conductivity changes slightly different, including Dinan mine samples grow slightly faster, Anyuan mine samples and Longnan mine samples conductivity is similar, where the overall Longnan mine samples slightly smaller than Anyuan mine samples. The linear variation of the conductivity of the solution indicates that the variation of the conductivity is mainly determined by the drip addition of the leaching agent, and the different slopes of the three minerals are mainly caused by the different ions involved in the exchange of the internal structure of the slip surface. At the beginning, the

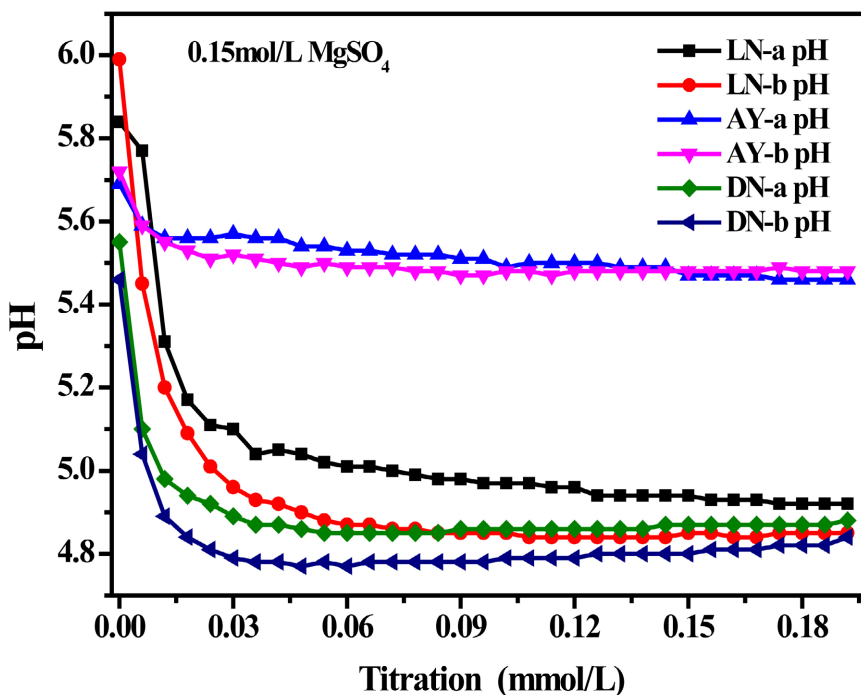


Figure 4. The relationship between leaching agent concentration and pH variation.

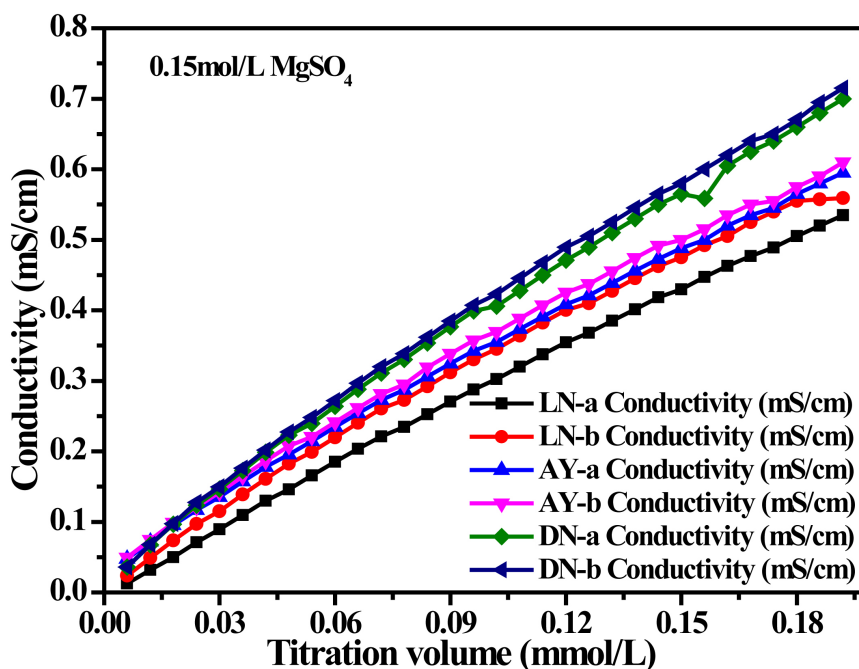


Figure 5. Variation of leaching agent concentration versus conductivity.

conductivity of all three mineral samples is small, indicating that the clay minerals have very few ions adsorbed on the surface and thus dissociate very little charge in solution, further indicating the greater stability of the internal structure of the slip surface of the clay minerals.

From **Figure 6**, the relationship between the content of rare earth ions and the concentration of leaching agent, it can be seen that the content of leached rare earth ions is the highest in Anyuan ore sample, followed by Dingnan, and the lowest in Longnan, where the amount of rare earth leached from Anyuan ore sample is about 2.5 times that of Longnan ore sample, which is different from the column leaching results. The content of the ore samples below 800 mesh was less than that of the generally larger granularity of the An Yuan ore samples. Combined with **Figure 2**, it can be seen that the leaching of rare earth ions existed in the process of dramatic change of pH and slow change of pH in the solution, which means that H^+ and OH^- in the solution were involved in the ion exchange between clay minerals and leaching agent at the beginning, and the pH of the solution with leaching agent did not change much during the ion exchange process afterward, and the balance of H^+ and OH^- was basically stable. Combined with **Figure 3**, the relationship between leaching agent concentration and conductivity changes shows that the conductivity is the largest in Dinan, the second largest in Anyuan and the smallest in Longnan, and the content of rare earth ions is the largest in Anyuan mine sample, the second largest in Dinan and the lowest in Longnan, indicating that some of the ions exchanged in Dinan mine sample may be other impurity ions, or it is possible that more leaching agent ions are adsorbed in Anyuan and Longnan mine samples.

From **Figure 7** Zeta potential versus rare earth ion content variation graph, it

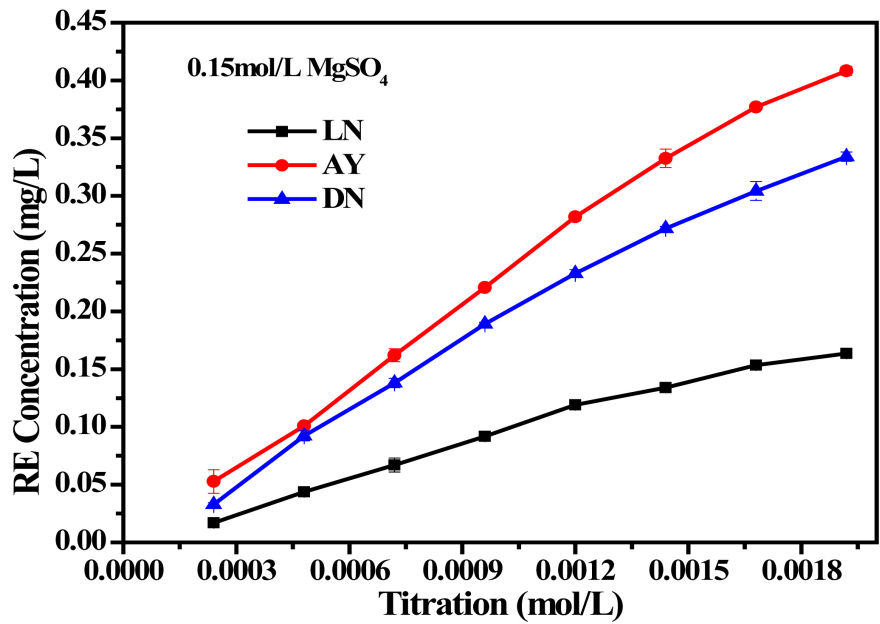


Figure 6. The relationship between the content of rare earth ions and the variation of leaching agent concentration.

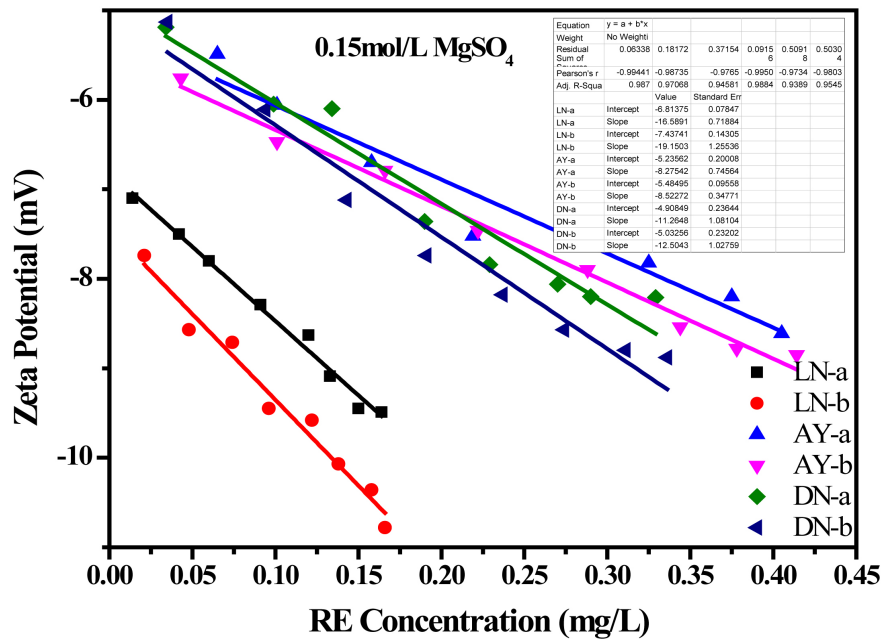


Figure 7. Zeta potential versus rare earth ion content.

can be seen that during the titration of 0.15 mol/L MgSO₄ leaching agent, its Zeta potential is linearly related to the leaching amount of rare earth ions, the larger the leaching amount of rare earth ions, the larger the absolute value of Zeta potential and the more negative the Zeta potential. The Zeta potential corresponds to the slip surface potential, where the rare earth ions are exchanged out of the slip surface by the leaching agent, and the positive charge inside the slip surface decreases and the negative charge increases due to the lower valence

of the exchanged ions, the presence of anions or poor bonding and rediffusion, etc. The linear relationship between the Zeta potential and the rare earth ion content indicates that the overall Zeta potential is negative. The linear relationship between Zeta potential and ion content indicates that the internal structural changes of the slip surface of clay minerals caused by the leaching of rare-earth ions are the main reason for the change of Zeta potential throughout the exchange process.

3.3. Evaluation of Correlation between Zeta Potential and Leaching Performance of Ammonium Sulfate Titration of Southern Clay Ore Samples

In the clay ore sample drip leaching system, pH is the result of the combined effect of the overall charge balance of clay minerals, ion dissociation balance and the formation of hydrogen bonds at the local fracture surface. As the concentration of the leaching agent increases gradually during the drip leaching process, the initial pH is not greatly influenced by the concentration of the leaching agent, and the change of pH is mainly expressed as the change of exchange process. The process is accompanied by a change in electrical conductivity. It can be seen that the internal structure of the slip surface of clay minerals determines the changes in pH, zeta potential and conductivity of clay mineral samples. The zeta potential is linearly related to the content of rare earth ions, so the change of zeta potential during the potentiometric dip leaching process can reflect the leaching performance of rare earths.

As shown in **Figure 8**, the pH of the leaching solution decreases with the drip of ammonium sulfate and then stabilizes with the drip of 1.50 N ammonium sulfate, the pH fluctuates after adding ammonium sulfate to 20 mL, and the zeta potential continues to decrease in **Figure 9**. The pH, zeta potential and conductivity are interrelated and are essentially influenced by the internal structure of the slip surface of the clay minerals. After adding 1.50 N ammonium sulfate to 20 mL drop by drop, and then adding ammonium sulfate drop by drop the conductivity remains unchanged, indicating that the ionic strength in the solution leads to no change, the reason is that the electrolyte concentration in the solution reaches a certain level and starts to compress the double electric layer, making some of the anions and cations into the interior of the double electric layer, of which more cations into the slip surface inside the Zeta potential negative value decreases, pH becomes smaller due to more cations are adsorbed. The pH and zeta potential of 1.50 N ammonium sulfate and 0.30 N ammonium sulfate dip can be corresponded to each other, and the solution pH is correspondingly larger for the larger negative value of zeta potential, which is because the larger the negative value of zeta potential inside the slip surface of clay minerals, the stronger its ability to combine with H^+ , and the larger the pH of increased OH^- in the solution. 0.30 N ammonium sulfate dip The decrease of the initial negative Zeta potential may be caused by the adsorption of cations by clay minerals under low-concentration electrolyte conditions. 0.03 N ammonium sulfate

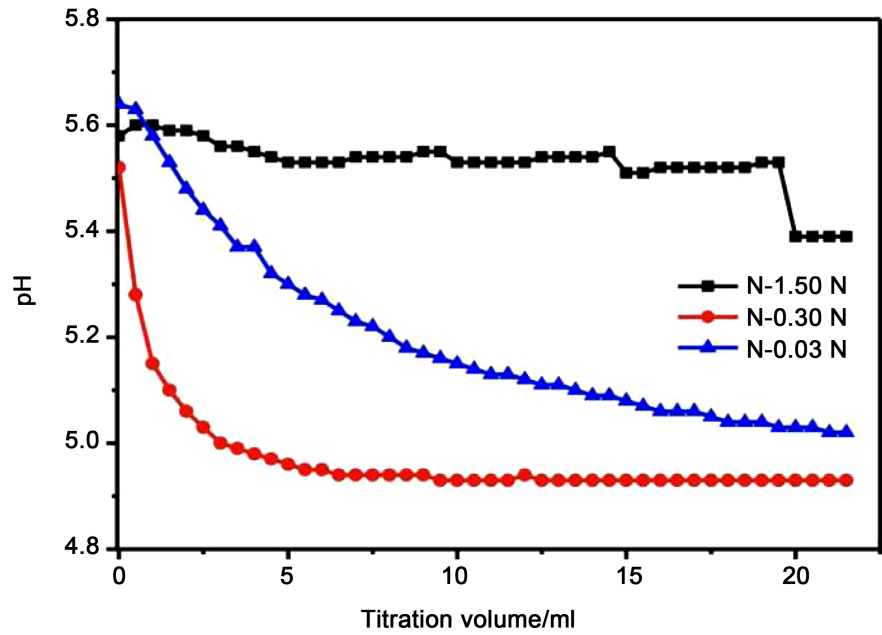


Figure 8. Graph of titration of ammonium sulfate versus pH change.

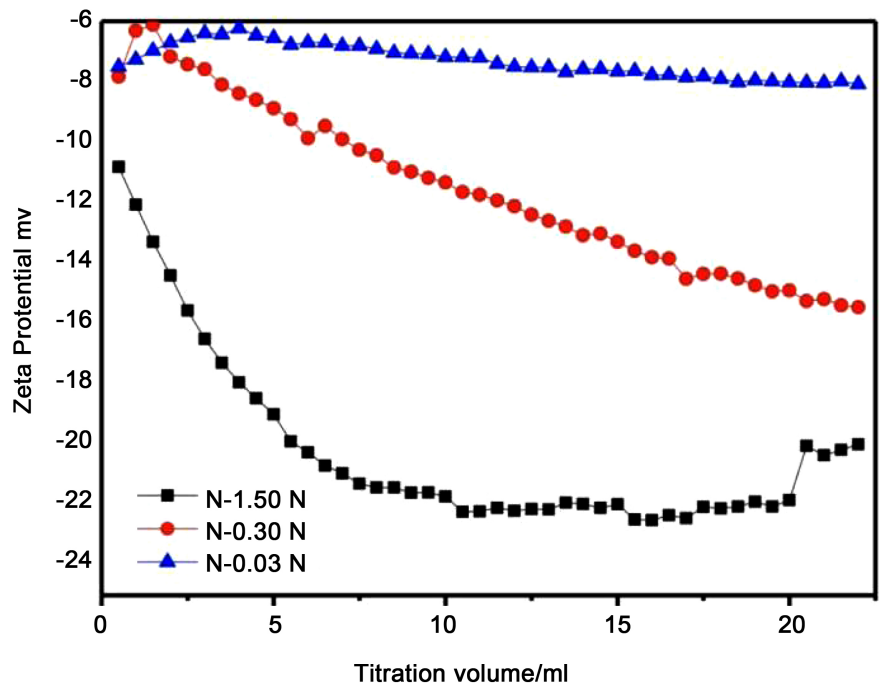


Figure 9. Ammonium sulfate titration versus zeta potential change.

dip corresponds to the low concentration electrolyte conditions, where clay minerals exhibit the adsorption process of cations rather than the ion exchange process, and the decrease of the negative Zeta potential of cations adsorbed by clay minerals, whose pH change may be to balance the solution charge, H^+ concentration increases pH decreases. As can be seen from Figure 10 and Figure 11, 1.50 N ammonium sulfate drops leaching in 10 mL after the rare earth content

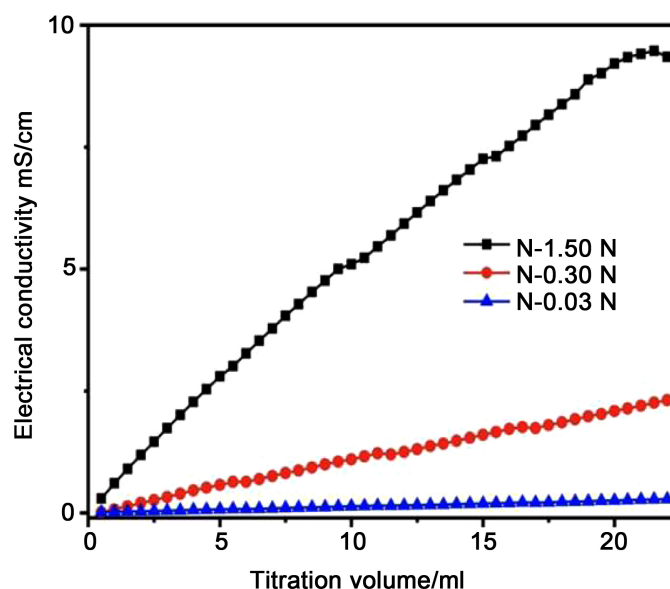


Figure 10. Ammonium sulfate titration versus conductivity change.

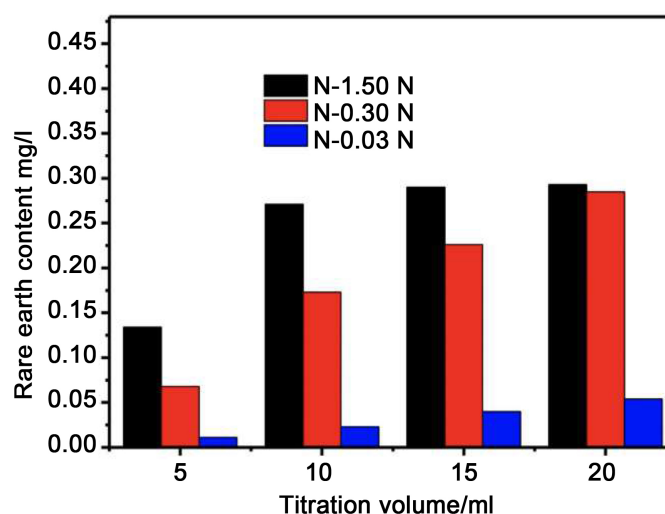


Figure 11. Relationship between changes in rare earth content.

almost unchanged, corresponding to its Zeta potential maintained stable; 0.30 N ammonium sulfate drop leaching process, rare earth content continued to increase, its corresponding Zeta potential absolute value continued to increase, corresponding to the leaching of rare earth ions; 0.03 N ammonium sulfate drop leaching process of rare earth ions leaching very little, its Zeta Potential and conductivity changes were not obvious.

3.4. Evaluation of Correlation between Zeta Potential and Leaching Performance of Southern Clay Ore Samples by Titration of Magnesium Sulfate

Through **Figure 12** leaching agent concentration and pH change relationship can be seen, with the magnesium sulfate leaching agent drop into the Dingnan

ore sample solution pH first reduced and then largely stable, combined with **Figure 13** can be seen 1.50 N and 0.30 N magnesium sulfate leaching agent drip leaching process Zeta potential negative value is large, the solution pH correspondingly larger, this is because the clay minerals in the slip surface Zeta potential negative value is larger, its and H^+ binding capacity, the stronger the solution of OH^- increase pH. The decrease of negative Zeta potential at the beginning of drip leaching is due to the adsorption of cations by clay minerals under low-concentration electrolyte conditions. 0.03 N drip leaching corresponds to the adsorption process of cations by clay minerals under low concentration conditions, rather than the ion exchange process, and the decrease of negative Zeta potential by clay minerals for adsorption of cations and the change of pH may be to balance the solution pH. The change may be to balance the charge in the solution,

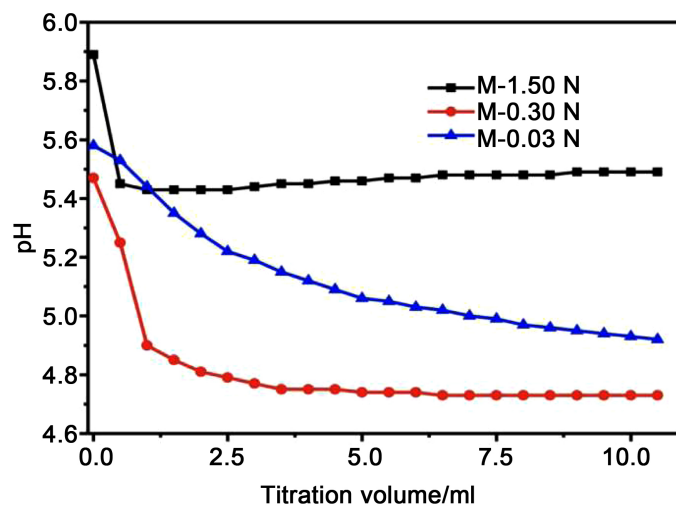


Figure 12. Titration volume of magnesium sulfate versus pH change.

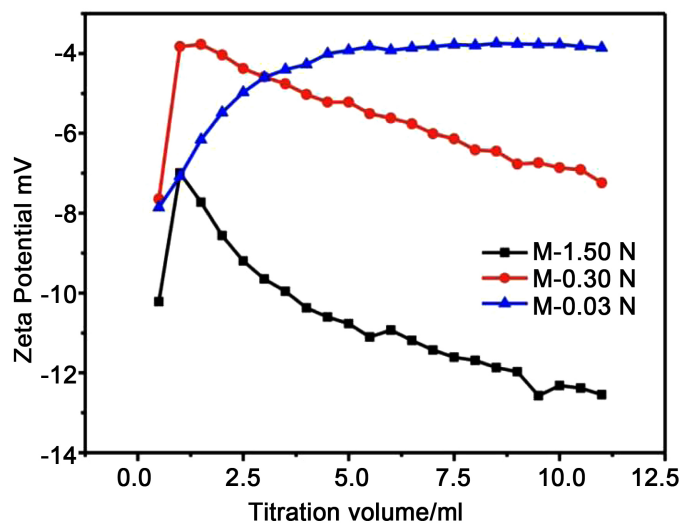


Figure 13. Titration volume of magnesium sulfate versus zeta potential change.

H⁺ concentration increases pH decreases. From **Figure 13** the relationship between the titration volume of magnesium sulfate and the change of conductivity, it can be seen that the conductivity tends to increase linearly with the drop of MgSO₄ leaching agent and the slope of different concentrations of magnesium sulfate is different, indicating that the change of solution conductivity is mainly determined by the drop of added magnesium sulfate, in the beginning, the conductivity of all three mineral samples is small, indicating that the clay minerals have very few ions adsorbed on the surface and thus dissociate very little charge in solution, further indicating the greater stability of the internal structure of the clay mineral slip surface. From **Figure 14** and **Figure 15**, it can be seen that the rare earths obtained by 0.03 N magnesium sulfate drop leaching are extremely small, and the amount of rare earths leached by 1.50 N and 0.30 N magnesium sulfate drop leaching are close to each other, and the comparison of their zeta potential changes shows that their zeta potential changes are similar and the change rate is similar when they obtain similar content of rare earths.

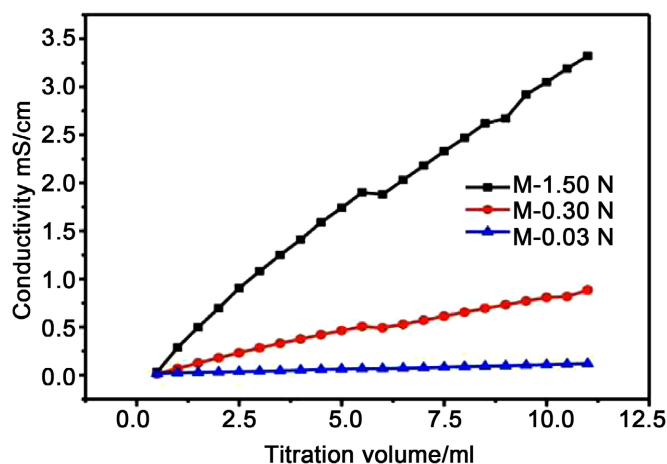


Figure 14. Titration volume of magnesium sulfate versus conductivity change.

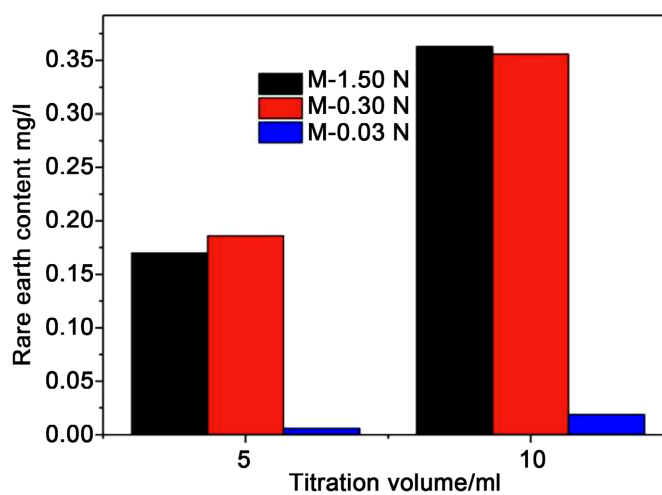


Figure 15. Relationship between changes in rare earth content.

3.5. Evaluation of Correlation between Zeta Potential and Leaching Performance of Aluminum Sulfate Titration of Southern Clay Ore Samples

Combined with **Figure 16** and **Figure 17**, it can be seen that the pH of the solution of the Dinan ore sample changes in two different trends as the aluminum sulfate leaching agent drips into the solution. This is because the larger the negative value of Zeta potential in the slip surface of clay minerals, the stronger their ability to bind H^+ , which shows the exchange process of clay minerals under higher concentration conditions, and their Zeta potential changes rapidly, indicating the strong exchangeability of aluminum sulfate under 1.50 N aluminum sulfate dip conditions. From **Figure 18**, the relationship between the volume of aluminum sulfate titration and the change of conductivity can be seen, with the aluminum sulfate leaching agent drop into the conductivity is a linear increasing trend and the slope of different concentrations of sulfuric acid rate is different,

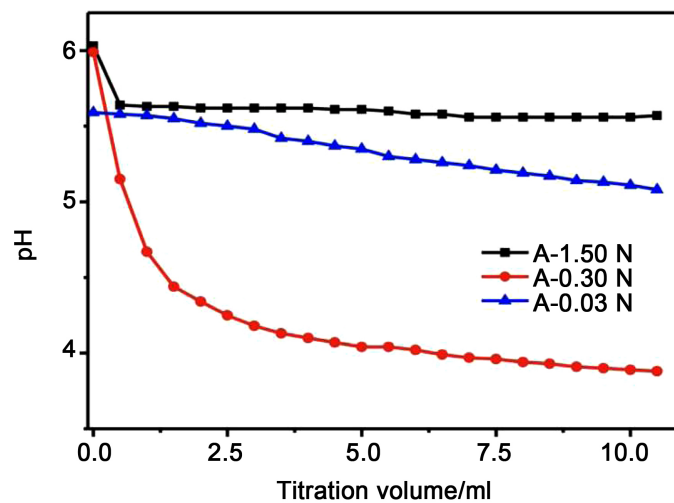


Figure 16. Plot of leaching agent concentration versus pH change.

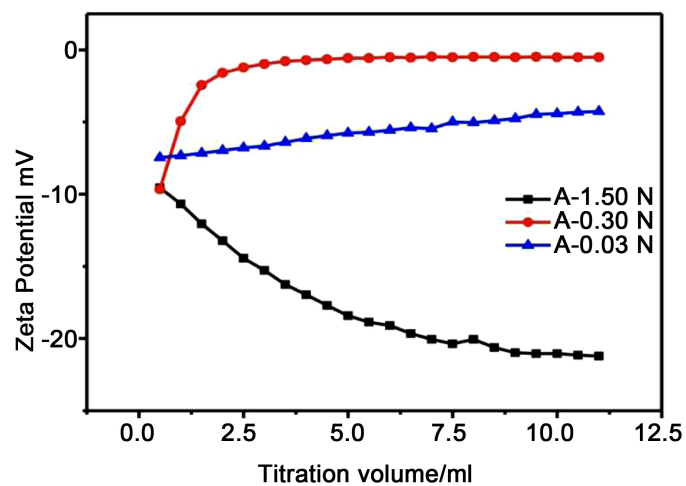


Figure 17. Relationship between leaching agent concentration and zeta potential variation.

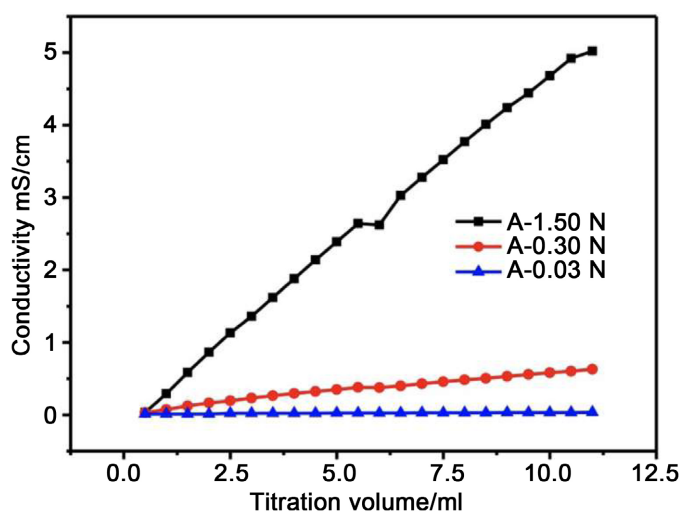


Figure 18. Plot of leaching agent concentration versus conductivity.

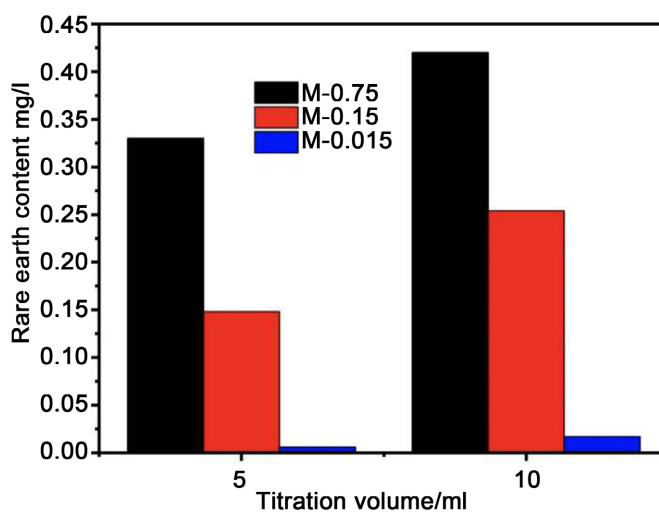


Figure 19. Relationship between changes in rare earth content.

indicating that the change of solution conductivity is mainly determined by the drop of added aluminum sulfate, at the beginning, the conductivity of all three ore samples are small, indicating the stability of the internal structure of the clay mineral slip surface. From **Figure 19**, it can be seen that the rare earth obtained by 0.03 N aluminum sulfate drop leaching is very little, and the rare earth leached out by 1.50 N and 0.30 N aluminum sulfate drop leaching, comparing their zeta potential changes, it is found that the rare earth obtained by 1.50 N drop leaching process corresponds to the zeta potential change, but the rare earth obtained by 0.30 N drop leaching process is different from the zeta potential change.

4. Conclusions

By quantitatively adding the leaching agent to the clay minerals dropwise and continuously measuring their zeta potential, pH and conductivity as well as tak-

ing samples to determine the rare earth content in the solution, it was found that the variation of zeta potential was related to the leaching content of rare earth ions and was linearly correlated, and the more rare earth ions were leached, the more negative zeta potential was. The relationships between the changes of Zeta potential, pH and conductivity of the three leaching agents, ammonium sulfate, magnesium sulfate and aluminum sulfate, at different concentrations of drop leaching clay ore samples were further investigated. It was found that the adsorption of cations by clay minerals existed at lower concentrations, and only at higher concentrations did they exhibit ion exchange properties. By the variation of zeta potential, it was found that different ion equivalent concentrations of low leaching effect, leaching agent at 1.50 N condition drip leaching, aluminum sulfate has the strongest leaching capacity, ammonium sulfate is the second, magnesium sulfate is weaker, leaching agent at 0.30 N condition drip leaching, magnesium sulfate has the strongest leaching capacity, ammonium sulfate is the second, aluminum sulfate shows a strong adsorption, leaching agent at 0.03 N Ammonium sulfate, magnesium sulfate and aluminum sulfate all exhibit adsorption.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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