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## Effect of polyacrylamide on the process of removing impurities in the rare earth leachate

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**Abstract:** The removal of impurities of the rare earth (RE) leachate from the RE-containing ore is usually accompanied by the formation of flocs, and a certain amount of polyacrylamide (PAM) flocculant needs to be added in this process. However, few studies have investigated the effect of the flocculant on the impurity removal process of the RE leachate. Therefore, this study aimed to investigate the flocculation process for removing impurities from the RE leachate in the absence and presence of PAM. The results showed that the addition of PAM showed little effect on the removal efficiencies of impurities, but it could increase the recovery of RE. And cationic PAM was more suitable for this impurity removal process than anionic PAM. When ammonium bicarbonate was firstly adopted to regulate the solution pH to 5.0, and then sodium sulfide was used to adjust the pH to 5.2, and 2 mg/L of cationic PAM was added to the solution, 96% Al<sup>3+</sup> and 98% Zn<sup>2+</sup> were removed from the solution, while 96% RE was maintained. Also, cationic PAM could accelerate the settlement of flocs, the settling time of the flocs shortened from 60 min to 20 min. This work may provide a promising way to shorten the production cycle and increase the recovery of RE.

**Keywords:** rare earth leachate, impurity removal, polyacrylamide, flocs

### 1. Introduction

The rare earth elements, closely related to the hi-tech industry, are used in the manufacturing of high strength permanent magnets, lasers, and electronic devices (Gupta and Krishnamurthy, 2005; Moldoveanu and Papangelakis, 2016; Cánovas et al., 2018). The rare earth (RE) can be extracted from the ore containing rare earths, such as phosphogypsum, mine tailings, etc. (Habashi, 1985; Chi and Tian, 2008; Hammas et al., 2016; He et al., 2016a; Hamza et al., 2019). According to the previous researches (Jarosinski et al., 1993; Hammas et al., 2016; Xiao et al., 2016; Feng et al., 2018), RE in the ore can be leached into the solution through leaching method. Subsequently, the leached RE can be recovered by precipitation method by ammonium bicarbonate or oxalic acid (Tian et al., 2011; Tian et al., 2013a; Hamza et al., 2019).

However, the Al<sup>3+</sup> and Zn<sup>2+</sup> in some ores will enter into the solution together with RE, and then affect the RE precipitation rate and increase the consumption of precipitants (Chi and Wang, 2014; Hamza et al., 2019). Therefore, it is essential to remove impurities in the RE leachate before the precipitation process. Chemical impurity removal method is commonly used to remove impurities due to its convenience and low cost (Zhang et al., 2016; Zhou et al., 2017; Hamza et al., 2019). Some research has been done in this area, and it has been found that ammonia, ammonium bicarbonate, and sodium sulfide can be used for the removal of impurities (Li and Chi, 1997; Kolar et al., 2016; Zhou et al., 2017). According to these studies, flocs, whose main component is aluminum hydroxide, will be formed in the impurity removal process (Luo et al., 2015). The flocs are very fine, and the filtration speed is slow.

Flocculation is a process in which small particles suspended in solution aggregate into larger aggregates, thus accelerating particle sedimentation and making filtration easier (Jarvis et al., 2005; Tadros, 2013; John, 2016; Moruzzi et al., 2017). Generally, some polyacrylamide (PAM) flocculant is added to improve the operation effect of the filtration process (Chi and Tian, 2008). While existing research only points out that the addition of PAM is beneficial to the settlement of flocs, and there is little research on the influence of the PAM on the impurity removal process.

Thus, in this study the effect of PAM on the flocculation process was investigated by comparing the effect of removing impurities before and after the addition of PAM. Additionally, the reasons for these effects were explained by analyzing the flocculation mechanism of PAM.

## 2. Materials and methods

### 2.1. Materials

Ammonium bicarbonate, sodium sulfide, anionic PAM, zinc oxide, ethylenediamine tetraacetic acid disodium, ascorbic acid, sulfosalicylic acid, xylenol orange, hexamethylenetetramine, hydrochloric acid, ammonium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) of analytical grade. Cationic PAM was supplied by Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China). Standard solution of zinc was purchased from National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials. The molecular weights of anionic PAM and cationic PAM were  $3.0 \times 10^6$  and  $1.2 \times 10^7$ , respectively. All the solutions were prepared with de-ionized water. The sample of the RE leachate was collected in the leachate recovery tank of a RE-containing mine in Yunnan Province, China. The contents of  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$  in the solution were  $0.175 \text{ g/dm}^3$  and  $1.85 \text{ mg/dm}^3$ , respectively, while the RE concentration was  $0.295 \text{ g/dm}^3$ , and the pH was 4.29.

### 2.2. Methods

#### 2.2.1. Removing impurities experiment

A  $100 \text{ cm}^3$  of RE leachate was mixed with different dosages of 7.9%  $\text{NH}_4\text{HCO}_3$ , 5%  $\text{Na}_2\text{S}$ , and 0.1% PAM in each measurement. The solution was mixed by a magnetic stirrer (MS-S, Shanghai) with a speed of 500 r/min. The reagents were added in the order of  $\text{NH}_4\text{HCO}_3$ ,  $\text{Na}_2\text{S}$ , and PAM. After reacting for 30 min, the solutions were filtered with  $0.22 \mu\text{m}$  filters, and then analyzed to calculate the recovery of RE, the removal efficiencies of  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$ . The ambient temperature was  $21 \pm 1 \text{ }^\circ\text{C}$ .

#### 2.2.2. Sedimentation experiment

A  $100 \text{ cm}^3$  of RE leachate was purified with a certain amount of 7.9%  $\text{NH}_4\text{HCO}_3$ , 5%  $\text{Na}_2\text{S}$ , and 0.1% PAM in each measurement. And, then the solution was transferred into the  $100 \text{ cm}^3$  measuring cylinder, and allowed to settle for a certain time, and then a syringe was used to take a sample of the supernatant from about 50 mm below the liquid level to determine the turbidity (Hach 2100q, USA) and zeta potential (Zetersizer Nano ZS980, Malvern, UK) of the solution. The experiments were conducted at an ambient temperature of  $21 \pm 1 \text{ }^\circ\text{C}$ .

#### 2.2.3. Analytical methods

The  $\text{RE}^{3+}$  contents in the solutions were analyzed by EDTA titration methods: use ascorbic acid to reduce ferric iron to ferrous iron and sulfosalicylic acid to mask ferrous iron. In the condition of using hexamethylenetetramine as buffer and xylenol-orange as indicator, titration analyzes the RE contents with EDTA. After that, excess EDTA solution was added into the studied liquid sample and placed in a water bath at  $90 \text{ }^\circ\text{C}$  for 10 min. Then the content of  $\text{Al}^{3+}$  was analyzed using back titration with a known concentration of zinc solution (Tian et al., 2013b; He et al., 2016b; Zhou et al., 2019). The concentration of  $\text{Zn}^{2+}$  was determined by an atomic absorption spectrometry (AA6300; Shimadzu, Japan). The RE recovery ( $\alpha$ ) and removal efficiencies of  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$  ( $\gamma$ ) were calculated using Eqs. 1 and 2, respectively:

$$\alpha = \frac{c_{RE}}{c_0} \times 100\% \quad (1)$$

$$\gamma_{Al/Zn} = \frac{C - C_{Al/Zn}}{C} \times 100\% \quad (2)$$

where  $\alpha$  and  $\gamma_{Al/Zn}$  are the RE recovery and removal efficiencies of  $Al^{3+}$  and  $Zn^{2+}$ , respectively; and  $C_{RE}$  and  $C_{Al/Zn}$  are the contents of  $RE^{3+}$  and  $Al^{3+}$  or  $Zn^{2+}$  after the impurity removal process; and  $C_0$  and  $C$  are the total contents of  $RE^{3+}$  and impurity ions of  $Al^{3+}$  or  $Zn^{2+}$  in the solution.

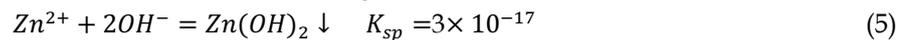
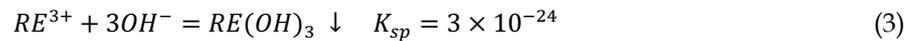
The zeta potential was measured by a laser particle sizer (Zettersizer Nano ZS980, Malvern, UK). The liquid sample was drawn with a syringe, and the sample was injected into the sample cell to measure the zeta potential, each sample was measured in triplicate. The measurement error was within  $\pm 0.5$  mV. The turbidity was analyzed using a turbidimeter (Hach 2100q, USA). First, the standard solutions with turbidity of 20 NTU, 100 NTU, and 800 NTU were used for the calibration of the turbidimeter, and then the liquid sample was added to the sample container for turbidity measurement. The measurement error was within  $\pm 1.0$  NTU.

### 3. Results and discussion

#### 3.1. Effect of removing impurities without the addition of PAM

##### 3.1.1. Behavior of $Al^{3+}$ and $Zn^{2+}$ in the impurity removal process

Impurity ions in RE leachate are usually removed in the form of hydroxide or sulfide precipitation. The possible chemical reactions are as follows:



For the hydroxide precipitates:



$$K_{sp} = [M^{n+}][OH^-]^n \quad (8)$$

$$K_w = [H^+][OH^-] \quad (9)$$

Then, the relationships between pM and pH are obtained as follows:

$$pM_{RE^{3+}} = 3pH - 18.48 \quad (10)$$

$$pM_{Al^{3+}} = 3pH - 9.11 \quad (11)$$

$$pM_{Zn^{2+}} = 2pH - 11.48 \quad (12)$$

For the sulfide precipitates, the relationship between pM ( $Zn^{2+}$ ) and pH can be also obtained by the same method as follows:

$$pM_{Zn^{2+}} = 2pH + 1.87 \quad (13)$$

The pM-pH diagram obtained from Equations (10)-(13) is shown in Fig. 1. From Fig. 1, the RE exists on the left of the black line and  $RE(OH)_3$  is on the other side. The  $Al^{3+}$  and  $Al(OH)_3$  are on the left and right of the red line, respectively. The precipitating pH of  $Al(OH)_3$  is 3.04 which is significantly lower than that of  $RE(OH)_3$ , suggesting that  $Al^{3+}$  can be removed as  $Al(OH)_3$  by controlling the pH of the solution, while the RE does not precipitate. However, the precipitation pH of  $Zn(OH)_2$  and  $RE(OH)_3$  is relatively close, and some RE will be lost if  $Zn^{2+}$  is removed in the form of  $Zn(OH)_2$ . Also,  $ZnS$  can be easily formed in the solution, while RE ions do not react with  $S^{2-}$  to form the sulfide precipitate. It can be seen from Fig. 1 that the purple line ( $ZnS$ ) is upper than the black line ( $RE(OH)_3$ ), indicating an efficient removing way of  $Zn^{2+}$  by sulfide precipitation method. Therefore, to reduce the loss of RE,  $Al^{3+}$  and  $Zn^{2+}$  can be removed in the form of  $Al(OH)_3$  and  $ZnS$ , respectively. That is to say, the pH of the solution should be increased, and a certain amount of sulfur ions should be provided in the impurity process.

Sodium sulfide ( $Na_2S$ ) is a sulfide commonly used in the industry. It is alkaline in an aqueous solution and can increase the pH of the system while providing sulfur ions. However, sulfur ions are unstable in acidic media and easily generate hydrogen sulfide. Therefore, it is necessary to first raise the pH of the solution and then add  $Na_2S$  to remove impurities, which can reduce the hydrogen sulfide

escape caused by weakly acidic RE leachate. Ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) and ammonia can be used to increase the pH of the solution, but considering the inconvenient transportation of ammonia in actual mine production,  $\text{NH}_4\text{HCO}_3$  is used to increase the system pH, and then  $\text{Na}_2\text{S}$  is added to remove impurities.

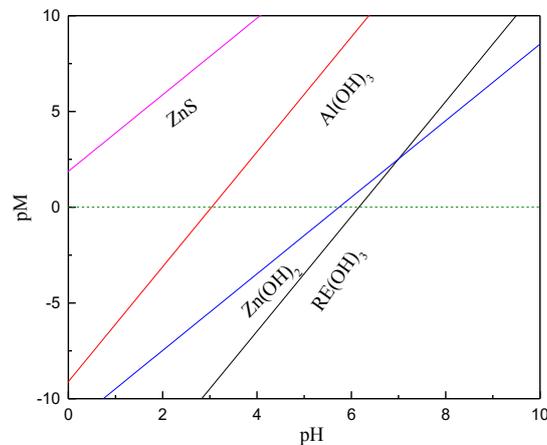


Fig. 1. pM-pH diagram of  $\text{RE}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Zn}^{2+}$  in the removal process for the impurities

### 3.1.2. Conditions for the impurity removal process with $\text{NH}_4\text{HCO}_3$ and $\text{Na}_2\text{S}$

According to the above analysis of the pM-pH diagram, it can be concluded that  $\text{NH}_4\text{HCO}_3$  should be added to the RE leachate first, and then  $\text{Na}_2\text{S}$  should be added to the solution to remove the impurities. Additionally, it can be seen from the pM-pH diagram seen in Fig. 1 that pH is a key factor affecting the removal of the impurities.  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  are alkaline in aqueous solution, and their addition will increase the pH of the solution. Therefore, the change of pH of the solution after the addition of  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  is usually used to represent their addition amount in industry. The optimal impurity removal conditions are those with higher impurity removal efficiency and RE recovery obtained by successively adjusting the pH of the solution using  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$ .

The optimized conditions for the removing impurities using  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  were studied to first adjust the pH of the solution to 4.6, 4.8, 5.0, and 5.2 by  $\text{NH}_4\text{HCO}_3$ , and then add  $\text{Na}_2\text{S}$  to the solution for impurity removal. The results are presented in Fig. 2(a)-(d), respectively. From Fig. 2, the  $\text{Zn}^{2+}$  removal efficiencies were maintained at a high level, exceeding 90%. Therefore, the optimum conditions were determined mainly by the RE recovery and  $\text{Al}^{3+}$  removal efficiency. As can be seen from Fig. 2(a)-(d), as the amount of  $\text{Na}_2\text{S}$  increased, the pH of the solution increased, the RE recovery decreased, and the  $\text{Al}^{3+}$  removal efficiency increased. In Fig. 2(a), when the pH of the solution was adjusted to 4.6 by  $\text{NH}_4\text{HCO}_3$ , then  $\text{Na}_2\text{S}$  was added to adjust the pH to 4.8, the RE recovery was 97% and  $\text{Al}^{3+}$  removal efficiency was 53%. At pH about 6.0, the RE recovery decreased to 81% and the  $\text{Al}^{3+}$  removal efficiency was up to 90%. From Fig. 2(b), at the pH around 5.0-5.2, RE recovery was about 90%, but the  $\text{Al}^{3+}$  removal efficiency was lower than 90%. In Fig. 2(c)-(d), when the pH of the solution was firstly adjusted by  $\text{NH}_4\text{HCO}_3$  to a high pH, the removal effect of  $\text{Al}^{3+}$  exceeded 90%, which was better than the removal effect of  $\text{Al}^{3+}$  in Fig. 2(a). However, the RE recovery decreased with increasing pH. To select appropriate conditions to meet the higher RE recovery and  $\text{Al}^{3+}$  removal efficiency, all the results presented in Fig. 2 were compared. It can be found that the optimum conditions were:  $\text{NH}_4\text{HCO}_3$  was firstly used to adjust the pH to 5.0, then  $\text{Na}_2\text{S}$  was adopted to regulate the solution pH to 5.2, 96%  $\text{Al}^{3+}$  and 98%  $\text{Zn}^{2+}$  were removed, while 93% RE was maintained under this condition.

As the process of removing impurities proceeds, white flocculent sediments appeared. In order to study the sedimentation of flocs in the process of removing impurities in the absence of PAM, the RE leachate was treated under the optimal conditions, and turbidity of the solution was measured. The results are shown in Fig. 3. It can be seen from Fig. 3 that the turbidity of the solution decreased rapidly with the increase of time, and then the decrease tended to be gentle. After settling down of the particles for 60 min, the turbidity of the solution basically remained around 27 NTU.

Based on the above analysis, it can be seen that after adjusting the pH of the RE leachate to 5.0 and 5.2 with  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$ , respectively, the removal efficiency of  $\text{Al}^{3+}$  was 96%, the removal efficiency of  $\text{Zn}^{2+}$  was 98%, and the RE recovery was 93%. The settling time of the flocs generated during the impurity removal process was 60 min, and the turbidity of the solution was about 27 NTU.

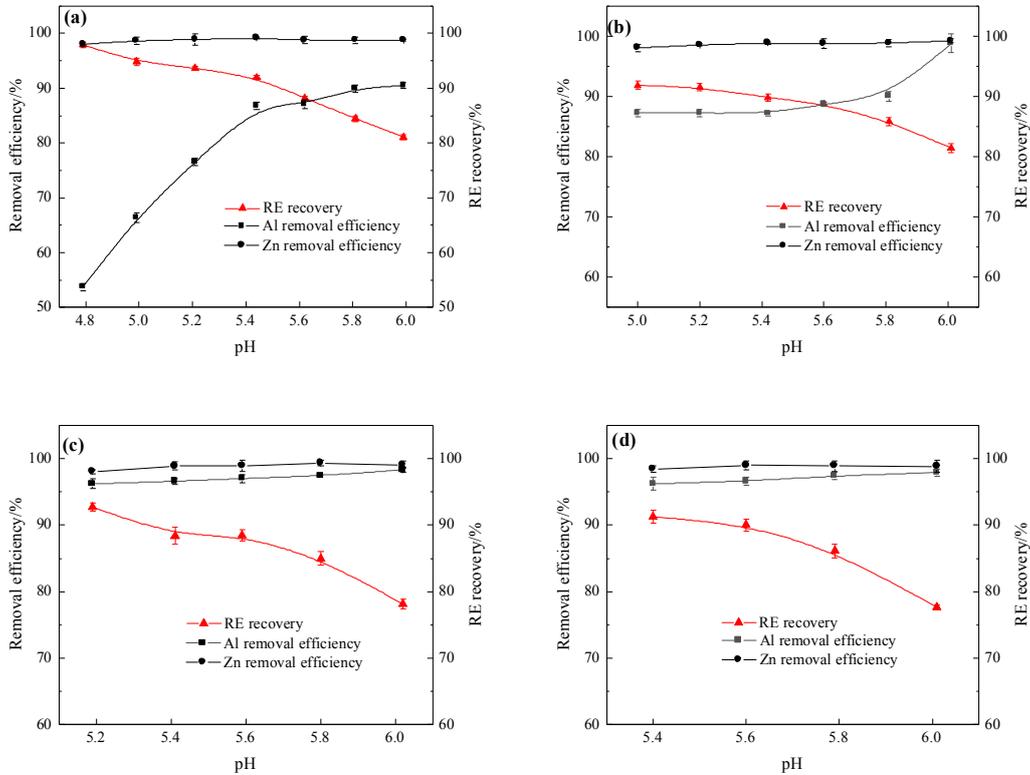


Fig. 2. Removal of impurities from RE leachate in the absence of the addition of PAM at pH of (a) 4.6 (b) 4.8 (c) 5.0 and (d) 5.2 adjusted by  $\text{NH}_4\text{HCO}_3$

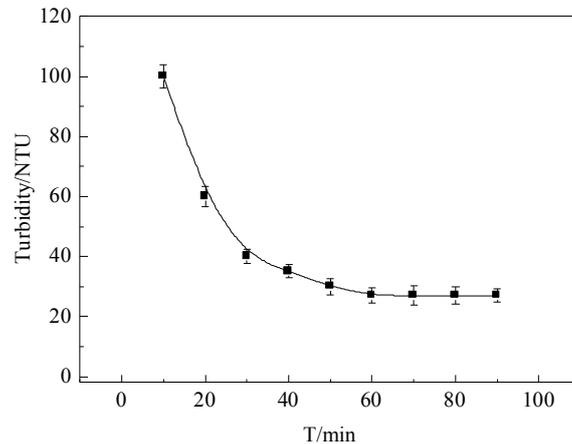


Fig. 3. Turbidity of the solution as a function of time in the absence of PAM

### 3.2. Effect of removing impurities with the addition of PAM

Flocculent precipitation was formed during the removal of impurities. The precipitate particles are very fine, the sedimentation speed is slow, the supernatant liquid has high turbidity, and the subsequent filtration will take a long time. Therefore, it can be considered to add flocculants in the process to accelerate its sedimentation. We studied the effect of PAM (anionic PAM and cationic PAM), a flocculant commonly used in industry, on this process. To study the influence of the addition of anionic PAM or cationic PAM on the effect of removing impurities,  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  were added to adjust

the pH of the solution to 5.0 and 5.2, respectively, and then different amounts of PAM were added. The results are shown in Fig. 4-7.

### 3.2.1. Effect of removing impurities with the addition of anionic PAM

Fig. 4 illustrates the effect of anionic PAM on the impurity removal process. As seen from Fig. 4(a) that the addition of anionic PAM showed less effect on the removal efficiencies of  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$ , but it could increase the recovery of RE. The optimal dosage of anionic PAM was 2 mg/L. At this time, the RE recovery was 95%, which was 2% higher than that without anionic PAM. The turbidity of the solution was measured after the floc had settled for 30 min. The results are shown in Fig. 4(b). As shown in Fig. 4(b), the solution turbidity initially decreased, and then increased with the increasing anionic PAM dosage. This might be because when the flocculant was added to the solution, the colloidal particles in the solution could be aggregated together through the long chain of the flocculant particles, and then the size of the colloidal particles would increase, and the sedimentation speed of the colloidal particles would increase, thereby lowering the turbidity of the solution. However, when the amount of flocculant was higher, the long chain of flocculant would completely cover the surface of the particles, preventing the colloid particles from flocculation (Gregory and Barany, 2011). And, then the turbidity of the solution would increase. Thus, the optimum dosage of anionic PAM was 2 mg/L.

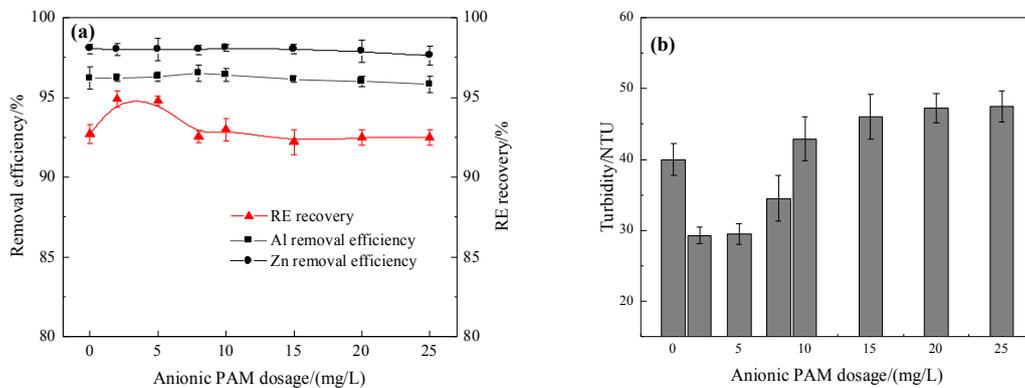


Fig. 4. Effect of anionic PAM dosage on (a) the impurity removal efficiency and (b) solution turbidity

To study the effect of adding anionic PAM on the sedimentation of flocs in the impurity removal process, the RE leachate was treated under the optimal conditions, that is, the  $\text{NH}_4\text{HCO}_3$  was firstly adopted to regulate the solution pH to 5.0, and  $\text{Na}_2\text{S}$  was used to adjust the pH to 5.2, and then 2 mg/L anionic PAM was added to the solution. The turbidity of solution under different settling time was measured, and the results are shown in Fig. 5. From Fig. 5, the turbidity of the solution decreased with the increase of the settling time. When the settling time was 40 min, the turbidity of the solution was maintained at about 24 NTU.

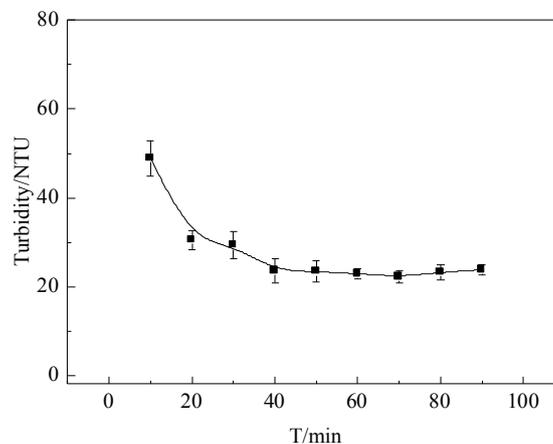


Fig. 5. Turbidity of the solution with the addition of 2 mg/L anionic PAM

It can be seen from Fig. 4 and Fig. 5 that after adding  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  to adjust the pH of the solution to 5.0 and 5.2, respectively, and then adding 2 mg/L anionic PAM to RE leachate, 96%  $\text{Al}^{3+}$  and 98%  $\text{Zn}^{2+}$  were removed, and 95% RE could be recovered. The settling time of the flocs generated during the impurity removal process was 40 min, and the solution turbidity was 24 NTU.

### 3.2.2. Effect of removing impurities with the addition of cationic PAM

Fig. 6 reveals the effect of cationic PAM on the impurity removal process. As shown in Fig. 6(a), there was almost no effect on the removal efficiencies of  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$ , while the RE recovery was affected. With the increase in the amount of cationic PAM, the RE recovery first increased and then gradually decreased. When the dosage of cationic PAM was 2 mg/L or 5 mg/L, the RE recovery was higher, about 96%. It can be seen from Fig. 6(b) that after 30 min of sedimentation, when the amount of cationic PAM was 2 mg/L, the turbidity of the solution was lower, about 15 NTU. Based on the above results, the optimum dosage of cationic PAM was 2 mg/L.

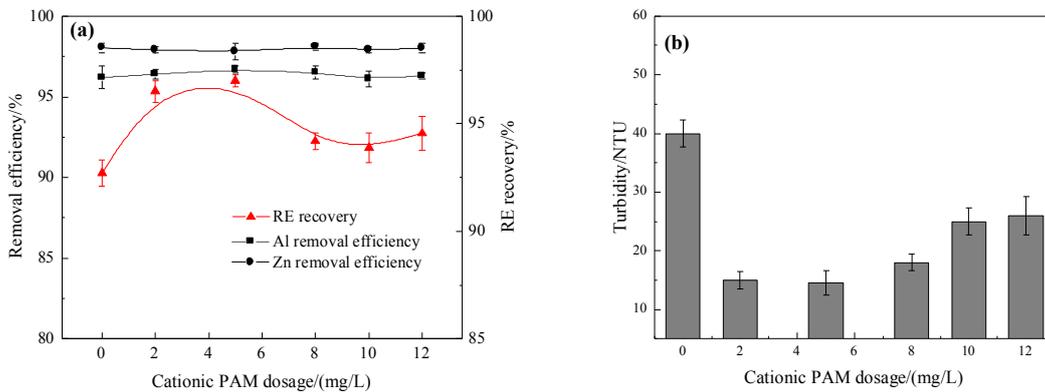


Fig. 6. Effect of cationic PAM dosage on (a) the impurity removal efficiency and (b) solution turbidity

To further study the time required for the flocs to settle under optimal cationic PAM dosage (2 mg/L), and turbidity of solution under different settling time was measured, and the results are shown in Fig. 7. From Fig. 7, the turbidity of the solution decreased rapidly in the first 10 min of settling, and then reached a plateau with the settling time increased from 10 min to 20 min to reach the lowest the turbidity of the solution. When the settling time was 20 min, the turbidity of the solution was about 15 NTU.

From Fig. 4 to Fig. 7, the flocculation effect of cationic PAM was better than that of anionic PAM in this system. The optimum conditions were:  $\text{NH}_4\text{HCO}_3$  was firstly used to adjust the pH to 5.0,  $\text{Na}_2\text{S}$  was adopted to regulate the solution pH to 5.2, and then 2 mg/L of cationic PAM was added to the solution, 96%  $\text{Al}^{3+}$  and 98%  $\text{Zn}^{2+}$  were removed from the solution, while 96% RE was maintained. Under this condition, the settling time of the flocs was 20 min and the solution turbidity was 15 NTU.

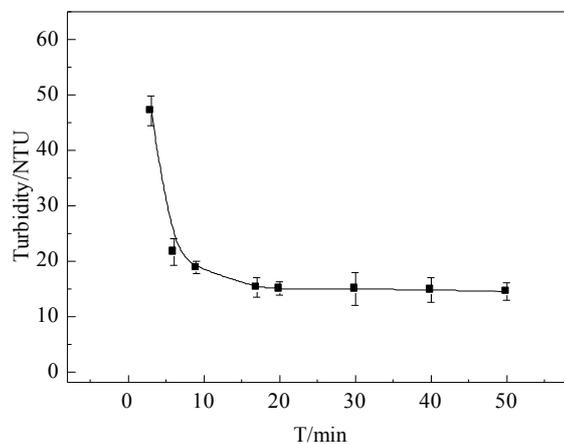


Fig. 7. Turbidity of the solution with the addition of 2 mg/L cationic PAM

### 3.3. Flocculation mechanism of PAM

After the comparison, it was found that the impact of PAM addition on the impurity removal process was mainly reflected in two aspects, increasing the RE recovery and shortening the settling time of flocs. Also, cationic PAM was more suitable for this impurity removal process. In order to better explain the cause of this phenomenon, it is necessary to analyze the flocculation mechanism of PAM.

The mechanism of the polymer flocculants generally includes bridge flocculation and electrical neutralization (Svarovsky, 2001; Besra et al., 2002). The schematic diagram is shown in Fig. 8. In this study, bridge flocculation mainly refers to that one end of the polymer chain of the PAM is adsorbed on a certain particle, and the other end free in the solution is adsorbed on the surface of another particle to form a "colloid-polymer-colloid" floc. The schematic diagram of bridge flocculation is shown in Fig. 8(a). From Fig. 8(b), when the added PAM and the particles in the solution have different charges, electrical neutralization will occur. The macromolecules adsorb onto the particles surface, neutralizing the surface charge thus reducing the thickness of the electrical double layer. Then, the agglomerates are created due to the action of van der Waals forces.

The zeta potential of the particles in the solution was measured, and the results are shown in Table 1. It can be seen from Table 1 that the zeta potential of the particles was -2.47 mV in the absence of PAM, while the zeta potential was still negative when the anionic PAM dosage was 2 mg/L (the optimum dosage). This indicates that the flocculation process is mainly based on the effect of bridge flocculation. Conversely, when 2 mg/L cationic PAM was added to the solution, the zeta potential of the particles changed from negative to positive. It can be concluded that the flocculation process is the result of the combined effect of bridge flocculation and electrical neutralization (Chang, 2011). Therefore, the flocculation effect of cationic PAM was better than that of anionic PAM in this system. When cationic generated floc has a specific adsorption effect on RE (Chi and Tian, 2008). When the settling time of the floc is shortened, the floc does not have enough time to adsorb more RE in the solution, thereby reducing the loss of RE in the solution and increasing the RE recovery.

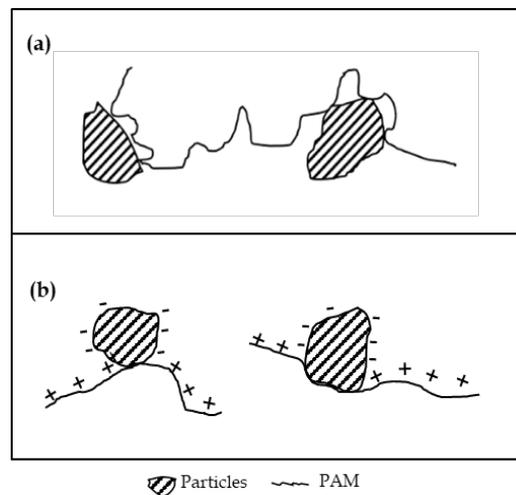


Fig. 8. Schematic diagram of (a) bridging flocculation and (b) charge neutralization

Table 1. The zeta potential of the particles in the solution in the absence and presence of PAM

Samples	PAM dosage/ (mg/L)	Zeta potential/mV
No flocculant <sup>1</sup>	0	-2.47
Anionic PAM <sup>2</sup>	2	-2.77
Cationic PAM <sup>2</sup>	2	0.41

<sup>1</sup> NH<sub>4</sub>HCO<sub>3</sub> was firstly used to adjust the pH to 5.0, Na<sub>2</sub>S was adopted to regulate the solution pH to 5.2

<sup>2</sup> NH<sub>4</sub>HCO<sub>3</sub> was firstly used to adjust the pH to 5.0, Na<sub>2</sub>S was adopted to regulate the solution pH to 5.2, and then PAM was added to the solution

#### 4. Conclusions

This study investigated the effect of polyacrylamide (PAM) on the impurity removal process of the RE leachate. The results showed that the use of PAM was beneficial to the recovery of RE in this process, and the cationic PAM was more suitable for this impurity removal process than anionic PAM. When  $\text{NH}_4\text{HCO}_3$  was used to adjust the solution pH to 5.0, and then  $\text{Na}_2\text{S}$  was added to regulate the pH to 5.2, and 2 mg/L of cationic PAM was added to the solution, 96%  $\text{Al}^{3+}$  and 98%  $\text{Zn}^{2+}$  were removed from the solution, while 96% RE could be recovered. Also, the addition of cationic PAM could accelerate the settlement of flocs, and the settling time was 20 min, which was shortened by 40 min. According to zeta potential analysis, the flocculation process was mainly based on the combined effect of bridge flocculation and electrical neutralization.

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#### References

- BESRA, L., SENGUPTA, D. K., ROY, S. K., AY, P., 2002. *Studies on flocculation and dewatering of kaolin suspensions by anionic polyacrylamide flocculant in the presence of some surfactants*. Int. J. Miner. Process, 66, 1-28.
- CÁNOVAS, C. R., MACÍAS, F., LÓPEZ, R. P., NIETO, J. M., 2018. *Mobility of rare earth elements, yttrium and scandium from a phosphogypsum stack: environmental and economic implications*. Sci. Total Environ., 618, 847-857.
- CHANG, Q., 2011. *Water treatment by flocculation*. Beijing: Chemical Industry Press.
- CHI, R. A., HU, Y., ZHU, G., XU, S., ZHOU, Z., XU, Z., 2003. *Solution-Chemistry Analysis of Ammonium Bicarbonate Consumption in Rare-Earth-Element Precipitation*. Metall. Mater. Trans B, 34B, 611-617.
- CHI, R. A., TIAN, J., 2008. *Weathered crust elution-deposited rare earth ores*. New York: Nova Science Publishers.
- CHI, R. A., WANG, D. Z., 1992. *Theoretical Analysis and Experimental Study on the Consumption of Oxalic Acid in the Rare Earth Precipitation Process of a Complex Solution*. Rare Earth (in Chinese), 13(4): 11-15.
- CHI, R. A., WANG, D. Z., 2014. *Rare Earth Mineral Processing*. Beijing: Science Press.
- FENG, J., ZHOU, F., CHI, R. A., LIU, X., XU, Y. L., LIU, Q., 2018. *Effect of a novel compound on leaching process of weathered crust elution deposited rare earth ore*. Miner. Eng., 129, 63-70.
- GUPTA, C.K., KRISHNAMURTHY, N., 2005. *Extractive Metallurgy of Rare Earths*. New York: CRC Press.
- GREGORY, J., BARANY, S., 2011. *Adsorption and flocculation by polymers and polymer mixtures*. Adv. Colloid Interface Sci, 169, 1-12.
- HABASHI, F., 1985. *The recovery of the lanthanides from phosphate rock*. J. Chem. Technol. Biotechnol., 35, 5-14.
- HAMMAS-NASRI, I., HORCHANI-NAIFER, K., FÉRID, Mokhtar., BARCA, D., 2016. *Rare earths concentration from phosphogypsum waste by two-step leaching method*. Int. J. Miner. Process, 149, 78-83.
- HAMZA, M.F., EL-AASSY, I.E., GUIBAL, E., 2019. *Integrated treatment of tailing material for the selective recovery of uranium, rare earth elements and heavy metals*. Miner. Eng., 133, 138-148.
- HE, Z. Y., ZHANG, Z. Y., YU, J. X., XU, Z. G., CHI, R. A., 2016a. *Process optimization of rare earth and aluminum leaching from weathered crust elution-deposited rare earth ore with compound ammonium salts*. J. Rare Earths, 34(4), 413-419.
- HE Z. Y., ZHANG Z. Y., YU J. X., ZHOU F., XU Y. L., XU Z. G., CHEN Z., CHI R. A., 2016b. *Kinetics of column leaching of rare earth and aluminum from weathered crust elution-deposited rare earth ore with ammonium salt solutions*. Hydrometallurgy, 163, 33-39.
- JAROSINISKI, A., KOWALCZYK, J., MAZANEK, C.Z., 1993. *Development of the Polish wasteless technology of apatite phosphogypsum utilization with recovery of rare earths*. J. Alloys Compd., 200, 147-150.
- JARVIS, P., JEFFERSON, B., GREGORY, J., PARSONS, S. A., 2005. *A review of floc strength and breakage*. Water Res., 39(14), 3121-3137.
- JOHN, B., 2016. *Coagulation and flocculation in water and wastewater treatment- third edition*. London: IWA Publishing.
- KOLAR, E., CATTHOOR, R.P., KRIEL, F.H., SEDEV, R., MIDDLEMAS, S., KLIER, E., HATCH, G., PRIEST, C., 2016. *Microfluidic solvent extraction of rare earth elements from a mixed oxide concentrate leach solution using Cyanex® 572*. Chem. Eng. Sci. 148, 212-218.

- LI, X. F., 2000. *Removing heavy metal ions from rare earth ore leachate by sodium sulfide*. Util. Miner. Resour (in Chinese), 3, 46-47.
- LI, X. F., CHI, R. A., 1997. *Study on removing impurities in the exchanged liquor of rare earth*. Comprehen. Util. Miner (in Chinese), 2, 10-13.
- LUO, X. P., ZOU, L. P., MA, P. L., LUO, C. G., XU, J., TANG, X. K., 2015. *Removing aluminum from a low-concentration lixivium of weathered crust elution-deposited rare earth ore with neutralizing hydrolysis*. Rare Met, 36 (8), 685-690.
- MOLDOVEANU, G. A., PAPANGELAKIS, V. G., 2016. *An overview of rare-earth recovery by ion-exchange leaching from ion-adsorption clays of various origins*. Mineral. Mag. 80(1), 63-76.
- MORUZZ, R. B., de OLIVEIRA, A. L., da CONCEICAO, F. T., GREGORY, J., CAMPOS, L. C., 2017. *Fractal dimension of large aggregates under different flocculation conditions*. Sci. Total Environ., 609, 807-814.
- SVAROVSKY, L., 2001. *Solid-Liquid Separation- fourth edition*. Oxford: Butterworth-Heinemann.
- TADROS, T., 2013. *Encyclopedia of Colloid and Interface Science*. Berlin: Springer Berlin Heidelberg.
- TIAN, J., YIN, J., CHEN, K., RAO, G., JIANG, M., CHI, R., 2011. *Extraction of rare earths from the leach liquor of the weathered crust elution-deposited rare earth ore with non-precipitation*. Int. J. Miner. Process, 3-4 (98), 125-131.
- TIAN, J., YIN, J. Q., TANG, X. K., CHEN, J., LUO, X. P., RAO, G. H., 2013a. *Enhanced leaching process of a low-grade weathered crust elution-deposited rare earth ore with carboxymethyl sesbania gum*. Hydrometallurgy, 139, 124-131.
- TIAN, J., TANG, X. K., YIN, J. Q., LUO, X. P., RAO, G. H., 2013b. *Process optimization on leaching of a lean weathered crust elution-deposited rare earth ores*. Int. J. Miner. Process, 119, 83-88.
- XIAO, Y. F., HUANG, L., LONG, Z. Q., FENG, Z. Y., WANG, L. S., 2016. *Adsorption ability of rare earth elements on clay minerals and its practical performance*. J. Rare Earths, 34, 543-548.
- YU, Q. H., ZHU, H. Y., LEI, H., LI, X. B., 1993. *Precipitation of rare earth carbonate from low grade leachate of rare earth ore*. Chin. Rare Earths, (in Chinese), 14, 14-17.
- ZHANG, L. Y., WU, Z. H., ZHANG, H. J., 1996. *Preparation of the mixed crystalline rare earth carbonate*. Chin. Rare Earths, (in Chinese), 17, 61-63.
- ZHOU, F., FENG, J., WANG, Z. Q., XU, Y. L., ZHANG, Z. Y., CHI, R. A., 2017. *One step purification of impurities in the leachate of weathered crust elution-deposited rare earth ores*. Physicochemical Problems of Mineral Processing, 53, 2, 1188-1199.
- ZHOU, F., LIU, Q., FENG, J., SU, J., LIU, X., CHI, R. A., 2019. *Role of initial moisture content on the leaching process of weathered crust elution-deposited rare earth ores*. Sep. Purif. Technol., 217, 24-30.