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Direct reuse of rare earth oxalate precipitation mother liquor for rare earth leaching

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Abstract: In the recovery process of rare earth (RE) from the weathered crust elution-deposited rare earth ore, ammonium sulfate is used as the leaching liquor to leach RE, and then the leachate containing RE³⁺ can be precipitated by oxalic acid and the RE oxalate precipitation mother liquor is reused for RE leaching process after removing the residual oxalic acid by precipitation with calcium hydroxide. However, the reuse process of precipitation mother liquor cannot proceed in the strong acid and alkali restricted areas and the discharge of mother liquor which contains a large amount of ammonium salt will cause ammonia-nitrogen waste and pollution. In order to realize the reuse of the precipitation mother liquor in this area, the direct reuse of RE oxalate precipitation mother liquor for RE leaching was investigated in this study. The RE oxalate precipitation process and the RE leaching process with oxalic acid were studied. The results showed that the residual oxalic acid concentration in the mother liquor can be controlled lower than 0.8 g/dm³ at pH 2-3 when the RE concentration in the leachate was 0.1-1.5 g/dm³ and the RE precipitation rate reached to 94%. In addition, RE leaching efficiency was up to 90% while the oxalic acid concentration in the prepared mother liquor was 0.2-0.8 g/dm³, pH 2-3. Therefore, the precipitation mother liquor with oxalic acid concentration less than 0.8 g/dm³ could be directly reused for RE leaching. However, considering the different performance of RE ores, the recommended oxalic acid concentration in the direct used precipitation mother liquor was lower than 0.6 g/dm³.

Keywords: weathered crust elution-deposited rare earth ore, oxalic acid, precipitation, mother liquor

1. Introduction

Weathered crust elution-deposited rare earth (RE) ore, known as the main resource of middle and heavy rare earth elements, has important commercial value and has been widely concerned by mining industry (Chen, 2011; Zhang et al., 2016; Feng et al., 2017). The minerogenic mechanism of this ore deposit relies on weathering of original rocks containing RE minerals into clay minerals such as kaolinite and montmorillonite. Meanwhile, RE in the original rocks are dissociated as hydrated or hydroxyl hydrated RE ions and further adsorbed on the clay minerals during the migration of water (Nesbitt, 1979; Tian et al., 2010; Li et al., 2015; Zhang et al., 2016). According to these characteristics, RE can be exchanged into solution with electrolyte solution by ion-exchange method (Huang et al., 2005; Moldoveanu and Papangelakis, 2013; Luo et al., 2015a; Luo et al., 2015b).

In the RE recovery process, ammonium sulfate is usually used as the leaching liquor to leach RE (Xiao et al., 2016), and then the leached RE can be recovered by precipitation reaction, and oxalic acid is one of the commonly used precipitants (Tian et al., 2013a; Tian et al., 2013b). The RE oxalate precipitation mother liquor still contains large amount of ammonium sulfate from the leaching liquor, its direct discharge will cause ammonia-nitrogen pollution and waste the remaining leaching liquor (Chi and

Wang, 2014; Qiu et al., 2014; Xiao et al., 2017). Therefore, the reuse of precipitation mother liquor has drawn attention of RE mining industry. However, when the precipitation mother liquor which still contains oxalic acid was used as the leaching liquor, the residual oxalic acid, especially of high concentration, may form RE oxalate and remain in the ore body, and then decrease the RE leaching efficiency. For this reason, the residual oxalic acid in the mother liquor is usually removed by precipitation with calcium hydroxide. However, this process cannot proceed in the area where strong acid and alkali are restricted. In order to realize the simple and efficient reuse of RE oxalate precipitation mother liquor in this area, the direct reuse of precipitation mother liquor was studied in this paper. To directly reuse the mother liquor from RE precipitation, it is necessary to ensure a low oxalic acid dosage in RE oxalate precipitation process while keeping high RE precipitation rate, so that the adverse effect of residual oxalic acid in the mother liquor on the RE leaching process can be ignored. Therefore, the RE oxalate precipitation process and RE leaching process under oxalic acid condition were studied to optimize the precipitation process and re-leaching process. This would provide a technical support for the reuse of RE oxalate precipitation mother liquor for RE leaching in the area where strong acid and alkali are restricted.

2. Materials and methods

2.1. Materials

The RE ore samples used in this study were collected from Dingnan City, Jiangxi Province, China, with the grade of 0.13%. Meanwhile, the RE leachate of this mine was used to investigate the direct reuse of RE oxalate precipitation mother liquor for RE leaching process. The RE concentration of the leachate was 0.558 g/dm³.

All chemicals used in this experiment were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) of analytical grade. All the solutions were prepared with deionized distilled water.

2.2. Column leaching and precipitation experiments

In the column leaching experiment, 250 g of RE sample was packed in a glass leaching column with an inner diameter of 50 mm and a length of 500 mm. Two pieces of filter papers were put on the top of the ore samples to ensure that the leaching liquor would contact with the ore uniformly. And then the leaching liquor was injected from the top of the leaching column with a peristaltic pump at a constant flow rate. The leachate was collected from the bottom of the column and the content of RE and pH were analyzed by ethylenediaminetetraacetic acid (EDTA) titration method and pH meter, respectively. The experiments were conducted at ambient temperature of 25 ± 0.5 °C.

The precipitation experiment was performed in the 500 cm³ beaker containing 200 cm³ RE leachate, and then oxalate acid was added in the leachate while stirring. After aging for 8 h, the solution was filtered, and then pH was measured with pH-meter and the content of RE and oxalic acid were analyzed by titration method. All the experiments were repeated at least three times. The experiments were conducted at ambient temperature of 25 ± 0.5 °C.

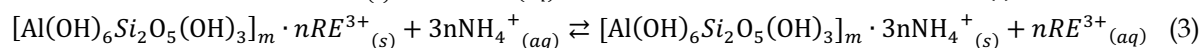
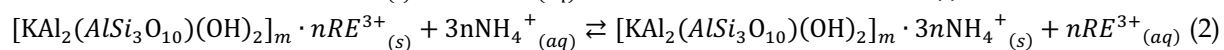
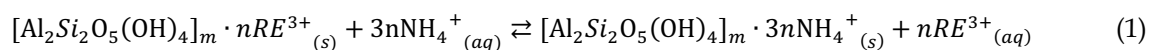
2.3. Analytical methods

The content of RE in the solution was analyzed by EDTA titration method (Zhou et al., 2017) by using xylenol orange as an indicator and hexamethylene tetramine as a buffer. The content of oxalic acid was tested by permanganate titration. The analysis was duplicated and the error of the titration method was within ±0.5%. The pH value of the solution was measured with pH-meter (DELTA320).

3. Results and discussion

3.1. Chemical foundation of RE leaching process

The RE ions and impurities adsorbed on clay minerals would be eluted into solution while the leaching liquor was injected to the orebody. This process follows the ion exchange rule. In the RE leaching process, when the clay minerals that adsorb RE ions are kaolinite, muscovite and halloysite, the following reactions occur (Tian et al., 2010; He et al., 2016a; He et al., 2016b):



where s and aq represent the solid phase and aqueous phase, respectively.

3.2. RE oxalate precipitation process

In industrial production, the dosage of oxalic acid is a vital factor affecting the recovery of RE since low oxalic acid consumption would lead to incomplete RE precipitation and overconsumption of oxalic acid would increase residual oxalic acid in the precipitation mother liquor and then decrease RE leaching efficiency when RE oxalate precipitation mother liquor is reused as the leaching liquor (Chi and Tian, 2008). Therefore, the control of oxalic acid dosage to realize the synergistic optimization of precipitation and re-leaching process are the key and difficult point in this study. Previous studies have shown that the concentration of RE in the leachate determines the dosage of oxalic acid (Tian and Yin, 1996). Therefore, the effect of RE concentrations of leachate on the dosage of oxalic acid was explored.

In the RE oxalate precipitation process, the dosage of oxalic acid is usually calculated as the molar ratio of oxalic acid and RE. The effect of oxalic acid dosage on RE precipitation rate, pH and residual oxalic acid at constant RE concentration is shown in Fig. 1. The theoretical molar ratio of $n(H_2C_2O_4 \cdot 2H_2O):n(RE^{3+})$ is 1.5:1 but in actual industrial production, the oxalic acid is used in an excess to ensure a high RE precipitation rate (Chi and Wang, 2014). Therefore, the precipitation mother liquor usually contains a large amount of residual oxalic acid. As can be seen from Fig. 1, to guarantee high RE oxalate precipitation rate (94%, an industrial demand), all the oxalic acid dosages for different concentrations of RE are higher than the theoretical amount of 1.5:1. With increasing oxalic acid dosage, the precipitation rate of RE increased rapidly and then was constant, while the residual oxalic acid concentration in the precipitation mother liquor gradually increased. At the same time, the changes in the concentration of oxalic acid and pH in Fig. 1 indicate that when RE leaching efficiency is over 94% in the tested RE concentration range, the residual oxalic acid in the precipitation mother liquor is lower than 0.8 g/dm³. Furthermore, the pH of precipitation mother liquor is maintained at 2-3 because of the buffer function of oxalic acid.

It can be concluded from the data in Fig. 1 that the dosage of oxalic acid is closely related to the concentration of RE in the leachate. When the RE precipitation rate was controlled over 94%, the oxalic acid dosage decreased as the concentration of RE in the leachate increased. The relationships between RE concentration and the dosage of oxalic acid when RE precipitation rate reached to 94% and the concentration of RE in the precipitation process for 1.9:1 molar ratio of oxalic acid to RE, were shown in Fig. 2.

When the dosage of oxalic acid was $n(H_2C_2O_4 \cdot 2H_2O):n(RE^{3+})=1.9:1$, the RE precipitation rate increased with the increase in RE concentration and then tended to be stable for the RE concentration higher than 1.0 g/dm³ (Fig. 2a). As it is visible in Fig. 2b, the required dosage of oxalic acid is reduced with the increasing concentration of RE (Tian and Yin, 1996). This phenomenon shows that the high RE concentration in the leachate makes RE precipitation easier with smaller amount of oxalic acid. Weathered crust elution-deposited rare earth ore is a special kind of mineral with a relatively low RE grade of 0.5-1.5% (Chi and Wang, 2014). The concentration of RE in the leachate is approximately 0.1-1.5 g/dm³ (Chi and Tian, 2008). Therefore, the minimum dosage of the oxalic acid can be selected according to RE concentration in the leachate to realize higher RE precipitation rate and lower residual oxalic acid.

3.3. Reuse of RE oxalate precipitation mother liquor for RE leaching

3.3.1. Reuse of prepared RE oxalate precipitation mother liquor for RE leaching

To investigate the effect of residual oxalic acid in the precipitation mother liquor on RE leaching efficiency, 2% ammonium sulfate containing oxalic acid was used as a leaching liquor to study reuse of RE oxalate precipitation mother liquor for RE leaching process.

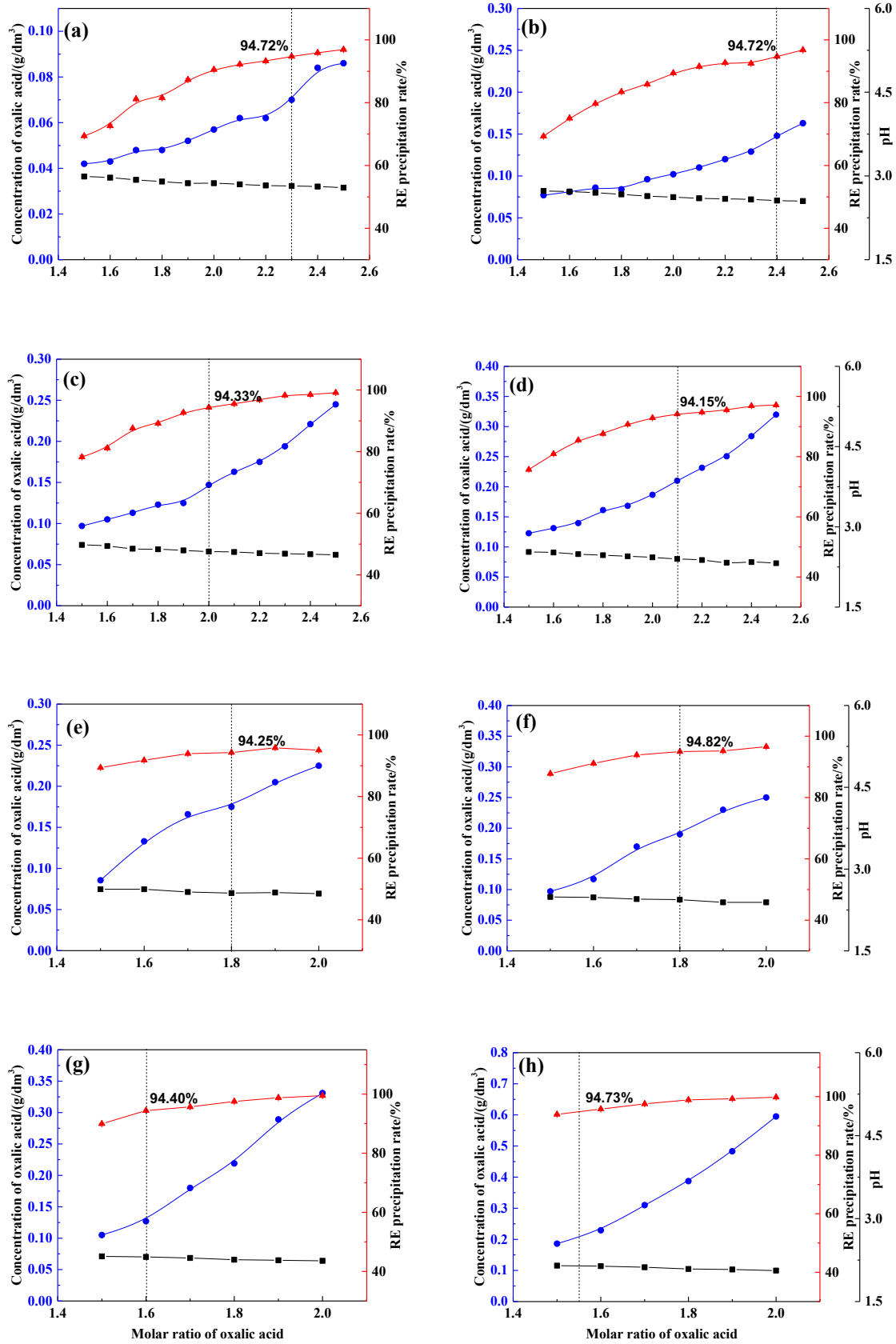


Fig. 1. Effect of the dosage of oxalic acid on RE precipitation rate (\blacktriangle), pH (\blacksquare) and residual oxalic acid concentration (\bullet) (RE concentration: (a) 0.102, (b) 0.209, (c) 0.311, (d) 0.420, (e) 0.521, (f) 0.815, (g) 1.000, (h) 1.540 g/dm³)

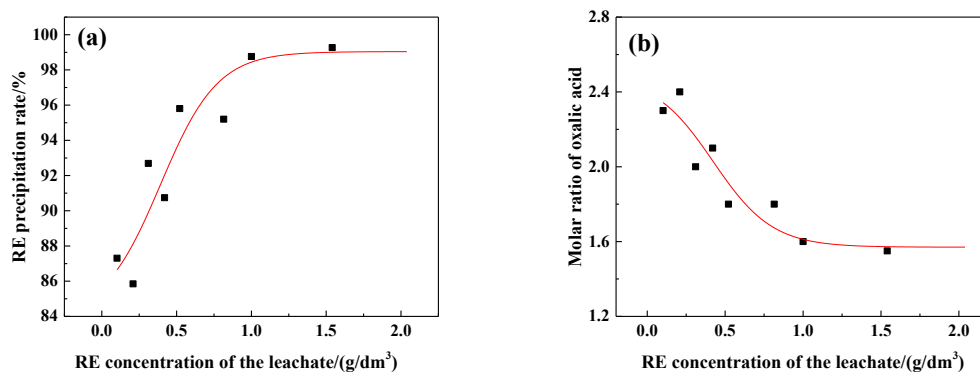


Fig. 2. Effect of RE concentration on (a) RE precipitation rate (dosage of oxalic acid to RE 1.9:1) and (b) oxalic acid dosage when RE precipitation rate reached 94%

3.3.1.1. Effect of oxalic acid concentration on RE leaching process

The effect of oxalic acid concentration on RE leaching process was investigated using 2% ammonium sulfate with oxalic acid under different concentrations of the mixed leaching liquor, and the results are shown in Fig. 3. It can be seen from Fig. 3 that RE leaching efficiency decreased with the increasing of oxalic acid concentration of leaching liquor, and the pH of leaching liquor decreased, too. When the oxalic acid concentration is 1.0 g/dm³, the pH is approximately 2.6 and the leaching efficiency drops below 90%. This result indicates that high concentration of oxalic acid in the leaching liquor will inhibit the leaching of RE, although the acidic environment is favorable for RE leaching process according to the literature (He et al., 2016b). However, due to the large amount of clay minerals contained in weathered crust elution-deposited rare earth ore, it has a certain acid-base buffering capacity (Li et al., 2012; Xiao et al., 2015), so that the pH of the leachate is maintained at 4.2-4.7.

From Fig. 3, it is further found that when 2% ammonium sulfate with oxalic acid concentration below 0.8 g/dm³ is used as the leaching liquor, the RE leaching efficiency is higher than 90%. This result indicates that oxalic acid less than 0.8 g/dm³ has little effect on the RE leaching efficiency. This may be due to the fact that partially ionized oxalate ions are adsorbed on the surface of RE ore and do not react with RE.

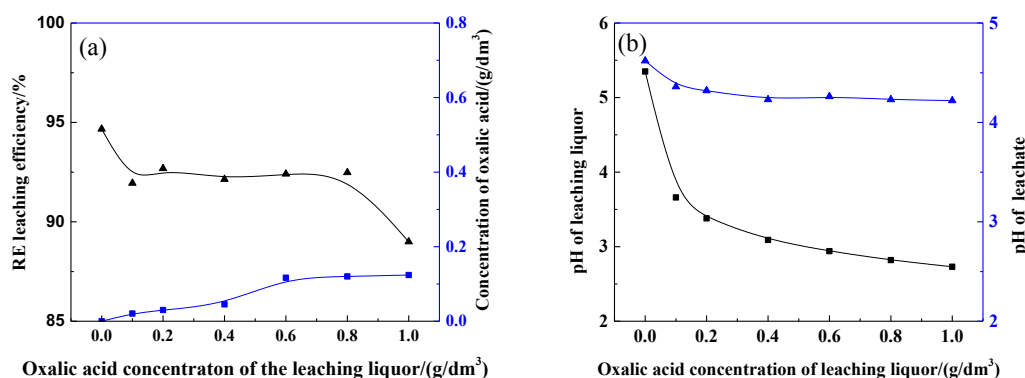


Fig. 3. Effect of oxalic acid on (a) RE leaching efficiency (▲) and oxalic acid concentration (■) in the leachate and (b) pH in the leaching liquor (■) and leachate (▲)

3.3.1.2. Effect of pH on RE leaching process

To investigate the effect of pH value on the oxalic acid leaching system, the mixture leaching liquor (i.e. 2% ammonium sulfate with oxalic acid) was used to re-leach rare earth ore and the results are shown in Fig. 4. Sulfuric acid and ammonium hydroxide were used as pH modifiers

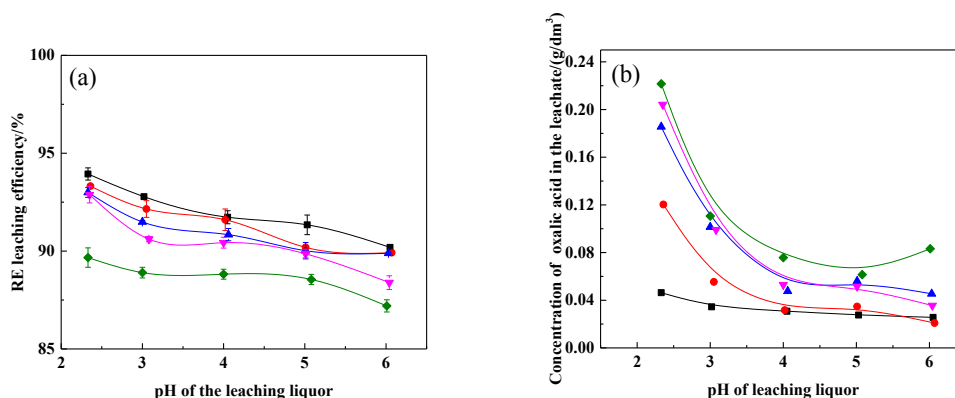


Fig. 4. Effect of pH on (a) RE leaching efficiency and (b) oxalic acid concentration in the leachate (concentration of the oxalic acid: (■) 0.2; (●) 0.4; (▲) 0.6; (▼) 0.8; (◆) 1.0 g/dm³)

RE leaching efficiency decreased with the increase of the pH value of the prepared precipitation mother liquor at constant concentration of oxalic acid (Fig. 4a). This is due to the fact that some of the colloidal phase of RE minerals dissolved in the strong acidic solution (pH < 4), and flew out with the leachate, increasing the content of RE in it (He et al., 2016b). The oxalic acid content in the leachate decreased with the pH of the leaching liquor (Fig. 4b), and for pH above 4 the acid concentration was constant. It was observed also that the oxalic acid content in the leachate was higher at pH of the leachate in the range between 2 and 4. This is because less $C_2O_4^{2-}$ would react with RE in the leaching process under strong acidic conditions, more oxalic acid enter leachate without reacting with the mineral. This shows that oxalic acid had weak inhibitory effect on RE leaching under strong acid leaching conditions, and little effect on RE leaching rate. This is consistent with the RE leaching rate results shown in Fig. 4a.

It can be inferred from Fig. 4 that for high pH and concentration of oxalic acid in the leaching liquor the leached RE could be precipitated with oxalic acid to form RE oxalate and remain in the ore body, hence, reducing the RE leaching efficiency and the concentration of oxalic acid in the leachate. When pH of the leachate ranged from 2 to 3, and the concentration of oxalic acid was lower than 0.8 g/dm³, oxalic acid had little effect on RE leaching efficiency, and RE leaching efficiency higher than 90% could be achieved in this study. This shows that the precipitation mother liquor can be directly reused as the leaching liquor for RE leaching process when the concentration of oxalic acid in this system is lower than 0.8 g/dm³.

3.3.2 Reuse of actual RE oxalate precipitation mother liquor for RE leaching

To confirm that the precipitation mother liquor containing a certain concentration of oxalic acid can be directly reused for RE leaching process, the actual RE leachate from the RE mine was collected to study the effect of oxalic acid dosage on RE precipitation and concentration of residual oxalic acid. The results are shown in Fig. 5. The actual mother liquor and prepared mother liquor were used as the leaching liquor for RE leaching, and the results are presented in Table 1.

As it is shown in Fig. 5, with the increasing oxalic acid dosage the RE precipitation rate and the residual oxalic acid increased, and the pH gradually decreased. When the oxalic acid dosage and the RE oxalate precipitation rate were 1.9:1 and 94.2%, the concentration of oxalic acid in the mother liquor amounted to 0.217 g/dm³ at pH 2.36. The precipitation mother liquor was then used as the leaching liquor to leach RE after a supplementation of ammonium sulfate with ammonium ions to 2% concentration of ammonium sulfate. The RE leaching efficiency yielded 96.2% which was similar to RE leaching efficiency of 94.7% when 2% ammonium sulfate was used as a leaching liquor.

Because of higher acidity in the actual mother liquor, the RE leaching efficiency of actual mother liquor was higher than that of the prepared mother liquor (Table 1). But both RE leaching efficiencies meet the needs of industrial production, which further confirms that it is feasible to reuse directly the RE oxalate precipitation mother liquor for RE leaching.

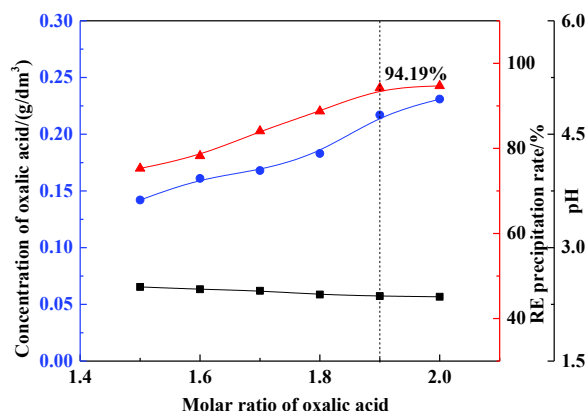


Fig. 5. Effect of dosage of oxalic acid on RE oxalate precipitation rate (\blacktriangle), pH (\blacksquare) and residual oxalic acid concentration (\bullet)

Table 1. Comparison of the RE leaching efficiency in different leaching conditions

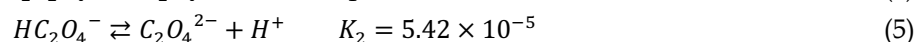
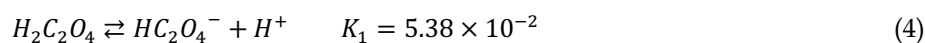
Leaching liquor	Concentration of oxalic acid /g/dm ³	pH	RE leaching efficiency / %
2% ammonium sulfate	0.000	5.43	94.7
Prepared precipitation mother liquor	0.217	3.21	92.4
Actual precipitation mother liquor	0.217	2.36	96.2

3.4. RE behaviour with oxalic acid in the RE leaching process

According to the previous results it can be summed up that RE leaching process is less affected when a certain amount of oxalic acid is added to the leaching liquor. In order to better understand this phenomenon, the species diagram (φ -pH) of oxalic acid and the reaction between RE and oxalic acid in the leaching process were analyzed.

3.4.1. φ -pH of oxalic acid in the aqueous solution

Oxalic acid is a dibasic weak acid, and secondary ionization occurs in aqueous solution. Its ionization expression is as follows:



K_1 and K_2 represent the first and second ionization constants of oxalic acid (Chi and Tian, 2008), respectively.

$$K_1 = \frac{c_{HC_2O_4^-} \cdot c_{H^+}}{c_{H_2C_2O_4}} \quad (6)$$

$$K_2 = \frac{c_{C_2O_4^{2-}} \cdot c_{H^+}}{c_{HC_2O_4^-}} \quad (7)$$

where $c_{HC_2O_4^-}$, c_{H^+} , $c_{C_2O_4^{2-}}$ and $c_{H_2C_2O_4}$ are the concentrations of $HC_2O_4^-$, H^+ , $C_2O_4^{2-}$ and $H_2C_2O_4$ in the solution, respectively.

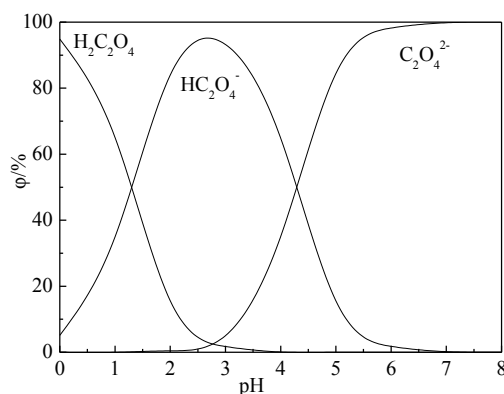


Fig. 6. Φ -pH diagram of oxalic acid in the aqueous solution

The total concentration of oxalic acid, containing three species, namely HC_2O_4^- , $\text{C}_2\text{O}_4^{2-}$ and $\text{H}_2\text{C}_2\text{O}_4$, can be expressed as

$$C = C_{\text{C}_2\text{O}_4^{2-}} + C_{\text{HC}_2\text{O}_4^-} + C_{\text{H}_2\text{C}_2\text{O}_4} \quad (8)$$

Then the fraction of each species can be calculated by the following Eqs.:

$$\varphi_0 = \frac{C_{\text{C}_2\text{O}_4^{2-}}}{C} = \frac{K_1 K_2}{C_{\text{H}^+}^2 + K_1 C_{\text{H}^+} + K_1 K_2} \quad (9)$$

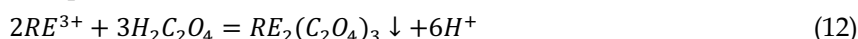
$$\varphi_1 = \frac{C_{\text{HC}_2\text{O}_4^-}}{C} = \frac{K_1 C_{\text{H}^+}}{C_{\text{H}^+}^2 + K_1 C_{\text{H}^+} + K_1 K_2} \quad (10)$$

$$\varphi_2 = \frac{C_{\text{H}_2\text{C}_2\text{O}_4}}{C} = \frac{C_{\text{H}^+}^2}{C_{\text{H}^+}^2 + K_1 C_{\text{H}^+} + K_1 K_2} \quad (11)$$

The calculated results are shown in Fig. 6, where $\text{H}_2\text{C}_2\text{O}_4$ is the predominant species at pH close to 0. At pH 3 and pH 7 the main species of oxalic acid are HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$, respectively.

3.4.2. Reaction between RE and oxalic acid in the leaching process

In the RE leaching process, RE ions adsorbed on clay minerals will enter the solution by ion-exchange method when ammonium salt is used as the leaching liquor. And then the leachate can be collected to recover RE. However, when the leaching liquor of ammonium sulfate contains a large amount of oxalic acid, the RE ions extracted by ammonium ions may react with oxalic acid to form RE oxalate precipitates. The precipitation reaction can be expressed as follows:



According to Equation (12), the RE oxalate precipitate is actually formed by the reaction of RE ions with $\text{C}_2\text{O}_4^{2-}$ ionized by oxalic acid. As it is shown in Fig. 6, the content of $\text{C}_2\text{O}_4^{2-}$ is directly related to the pH value of the solution. Due to the buffering effect of the clay mineral and oxalic acid, the pH in the leaching process is lower than 4.5 (Fig. 3 b). At this pH $\text{C}_2\text{O}_4^{2-}$ is not the main species of oxalic acid, which indicates that the amount of oxalic acid actually added in the leaching liquor does not completely interact with RE. Therefore, when an ammonium salt solution containing a small amount of oxalic acid is used as the leaching liquor, less $\text{C}_2\text{O}_4^{2-}$ is ionized, resulting in less precipitation of RE oxalate, which has insignificant effect on the RE leaching efficiency. Conversely, when large amounts of oxalic acid are added to the leaching liquor (Fig. 5), the amount of ionized $\text{C}_2\text{O}_4^{2-}$ will increase, and more RE oxalate will be formed, which seriously affects the RE leaching efficiency. Combined with the previous experimental results, RE leaching efficiency is less affected when the oxalic acid in the leaching liquor is kept below 0.6 g/dm^3 .

4. Conclusions

(1) The RE oxalate precipitation process was controlled to reach 94% RE oxalate precipitation rate for the leachate of $0.1\text{-}1.5 \text{ g/dm}^3$ RE concentration, while the residual oxalic acid concentration in the

precipitation mother liquor was kept lower than 0.8 g/dm³ which is beneficial to the reuse of RE oxalate precipitation mother liquor for RE leaching.

(2) When the oxalic acid concentration in precipitation mother liquor is lower than 0.8 g/dm³ and the solution pH is 2-3, the RE leaching efficiency reaches 90%. Therefore, the precipitation mother liquor with the oxalic acid concentration lower than 0.8 g/dm³ can be directly reused for RE leaching. However, the recommended oxalic acid concentration of reuse precipitation mother liquor is suggested to be lower than 0.6 g/dm³ on the account of the different performance of RE ores.

Acknowledgments

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