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Removing aluminum from a low-concentration lixivium of weathered crust elution-deposited rare earth ore with neutralizing hydrolysis

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Abstract Aluminum, the main impurity in the lixivium of weathered crust elution deposited rare earth ore, not only results in an increasing consumption of precipitant in the rare earth precipitation process, but also lowers the purity of final rare earth product. Aluminum in the weathered crust elution-deposited rare earth ore lixivium should be removed. Neutralizing hydrolysis method was employed to remove aluminum from the lixivium. Hexamethylenetetramine was found to be the optimum pH regulator for the removal of aluminum in the low concentration. When used to adjust the pH value of the lixivium to 5.0, aluminum in the lixivium can be effectively removed in the form of aluminum hydroxide precipitation with removal rate of 97.60 %. It shows that hexamethylenetetramine has a good effect on the removing of aluminum ions from the low-concentration lixivium. Moreover, hexamethylenetetramine in removing aluminum from lixivium has little adverse effect on the RE precipitation process.

1 Introduction

Weathered crust elution-deposited rare earth (RE) ore which mainly distributed in China is the main RE resource in the world [1]. It is rich in mid-heavy RE elements such as Sm, Eu, Gd, Dy, Lu, Y, etc. [2]. RE element in the ore exists mainly on the surface of clay minerals (such as nerchinskite, illite, kaolinite, smectite, quartz, and feldspar), referred to as ion-absorb phase RE [3, 4], which can be extracted only through chemical leaching method with its ion-exchangeable mechanism [5]. In leaching process, RE ions in the ore are desorbing and entering into lixivium. Subsequently, precipitation method (commonly using NH_4HCO_3 as pH regulator) is used to extract RE from the lixivium [4].

However, there are many aluminum ions whose properties are similar to those of RE ions in the ore [6]. In the leaching process, these aluminum ions are desorbing and entering into the lixivium together with RE ions [7]. In the follow-up RE precipitation process, these aluminum ions in the lixivium co-precipitate with RE ions [8]. The precipitated aluminum ions wrap on the surface of RE precipitation to make it form flocculent precipitation rather than crystalline precipitation. Compared to the crystalline precipitation, the flocculent precipitation has a particular larger volume, which is far more difficult to filter. Moreover, the existence of these precipitated aluminum ions lowers the purity of the final RE product. Thus, it is very essential to remove the aluminum ions from the lixivium before RE precipitation process [9–11], and solvent extraction is the most effective way to remove aluminum from the lixivium

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[12]. However, this method cannot be applied in practical aluminum removing due to its several defects (such as inconvenience operation and high cost) [12, 13]. At present, the common way for removing aluminum ions from the lixivium is neutralized hydrolysis method because of its prominent advantages of simple operation, low cost, and high efficiency in removing aluminum [13, 14]. The principle of this method is based on that the pH values of Al^{3+} and RE^{3+} forming hydroxide precipitation are different [15]. In the aluminum removing process, pH regulator (commonly using ammonium bicarbonate) is directly added into the lixivium in an appropriate portion to adjust the pH value to ~5.0. Under this condition, aluminum ions in the lixivium hydrolyze and form precipitation [16, 17]. Subsequently, the precipitation can be separated from lixivium by filtering. Commonly in practice, the removal rate of Al^{3+} is above 95 % and a small part (about 5 %) of RE in the lixivium would be loss [18].

However, when using this method to treat the RE lixivium with low concentration (<2 g·L^{-1}), the aluminum removal process is always associated with low removal rate (about 60 %–80 %) and high RE loss (about 15 %–20 %) [17]. Experimental evidence shows that the emergence of these problems are mainly as a result of the high ratio of Al^{3+}/RE^{3+} of the low-concentration lixivium [16, 18]. The most efficient way to solve the problem is to choose an optimal pH regulator to remove aluminum from the low-concentration lixivium [16].

Thus, in this paper, researches on removing aluminum ions from low-concentration lixivium were carried out. The pH regulators (ammonia, ammonium bicarbonate, hexamethylenetetramine, sodium acetate and sodium sulfide, respectively) which may have good effect on removing aluminum ions were chosen [13, 18]. Moreover, the optimum pH regulator to remove aluminum ions would be selected from the reagents above according.

2 Experimental

2.1 Materials

A low-concentration lixivium of a lean weathered crust elution-deposited RE ore (grade of 0.065 %, collected from Zudong Rare Earth Mine area located in Longnan County, Jiangxi, China) was used. The RE concentration of the lixivium determined by ethylene diamine tetraacetic acid (EDTA) volumetric titration method was 1.61 g·L^{-1}. The aluminum concentration of the lixivium determined by chromazurol S spectrophotometry method was 100.26 mg·L^{-1}.

2.2 Reagents

Unless otherwise stated, all chemicals used in aluminum removing experiments were of analytical reagent grade (as-receive without further purification). Moreover, deionized water was used in preparation of all the solutions in aluminum removing experiments. Reagents used in analysis of RE contents in the lixivium were acetylacetone, α-benzoin oxime hexamethylenetetramine, ascorbic acid, sulfosalicylic acid, EDTA and xylenol orange (Chemical Reagent Factory of Tianjin Damao, China). Reagents used in analysis of Al^{3+} content in the lixivium were chromazurol S, oxalic acid, perchloric acid, and ascorbic acid (Chemical Reagent Factory of Tianjin Damao, China).
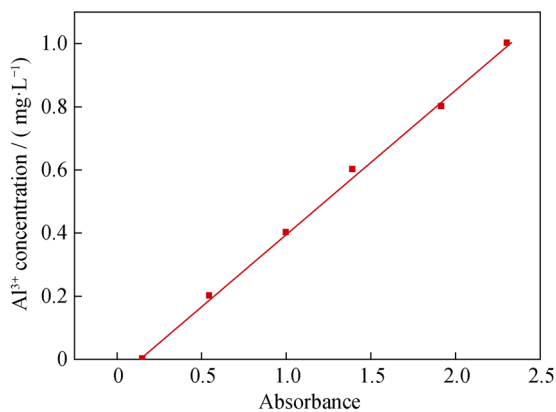
2.3 Analytical methods

The morphology of the RE products were measured by a scanning electron microscope (SEM, EVO-Zeiss Jena, Germany). The RE content in lixivium was determined by EDTA volumetric titration methods [19]: α-Benzoin oxime was used to precipitate the heavy metal ions, acetylacetone to mask aluminum ion in the lixivium, ascorbic acid to reduce ferric iron to ferrous iron and sulfosalicylic acid to mask ferrous iron. Using hexamethylenetetramine as buffer and xylenol orange as indicator, titration was carried out to analyze RE concentration with EDTA.

Al^{3+} concentration in lixivium was determined by chromazurol S spectrophotometry [20], which is based on the fact that Al^{3+} reacting with chromazurol S would from amaranthine clathrate in weak acidic environment (pH value of about 5.7). Oxalic acid was used to precipitate RE, perchloric acid fume to destroy the oxalic acid, ascorbic acid to reduce ferric iron and hydroxylamine hydrochloride
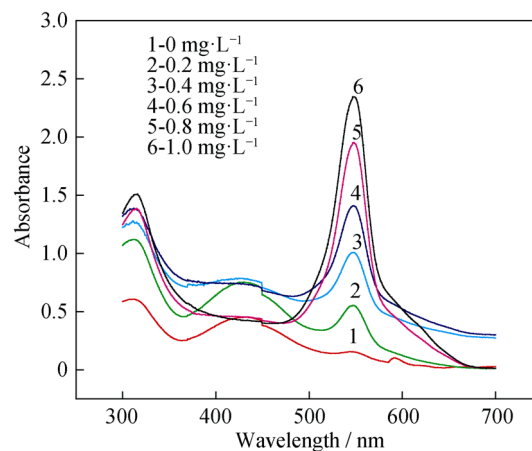
Fig. 1 Absorption spectra of clathrate generated by different concentrations of Al^{3+} reacting with chromazurol S

Fig. 2 Calibration curve of aluminum

Fig. 3 Existential form of aluminum (Al) and RE under various pH solutions (where $c_{Me^{n+}}$ being RE^{3+} and Al^{3+} concentrations in solutions)

to screen the residual RE. Figure 1 shows the absorption spectra of clathrate generated by Al^{3+} with different concentrations reacting with chromazurol S. Obviously, there are characteristic absorption peaks at wavelength of 545 nm. Thus, the calibration curves of aluminum can be drawn, as shown in Fig. 2).
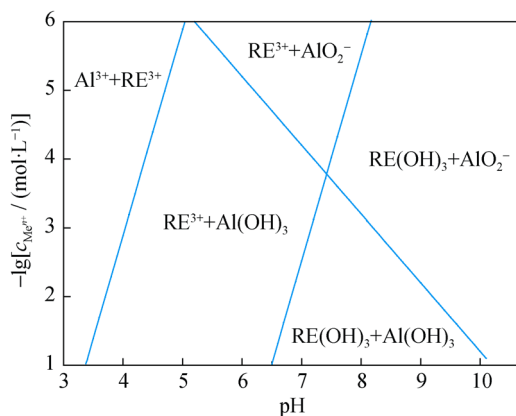
3 Results and discussion

3.1 Mechanism of removing aluminum from lixivium with neutralizing hydrolysis

The existing forms of aluminum (Al) and RE under various pH solutions are shown in Fig. 3 [13], which are different at some pH range. Clearly, when the pH value is below 5.4, aluminum in the lixivium is in the form of aluminum hydroxide precipitation. And when the pH value is higher than 4.4 and lower than 5.4, RE in the lixivium is in the form of ionic state. So, when using pH regulator to adjust the pH value of lixivium at 4.4–5.4, aluminum in the lixivium would hydrolyze and precipitate. Subsequently, it can be removed from lixivium by filter.
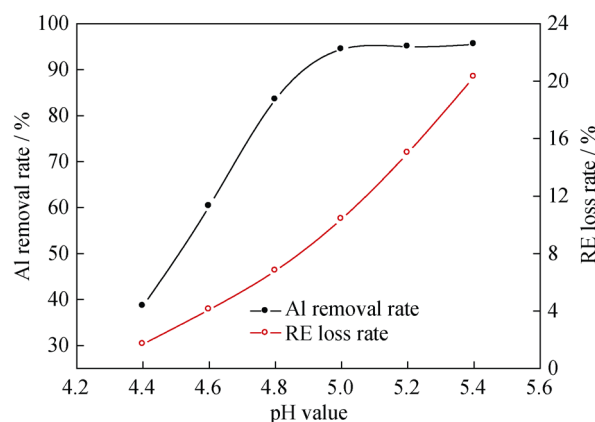
3.2 Effects of ammonia on removing aluminum

In this stage, ammonia is used as pH regulator to remove aluminum from lixivium. Ammonia with different dosages was added into lixivium at a uniform velocity to adjust pH value of lixivium to 4.4, 4.6, 4.8, 5.0, 5.2 and 5.4, respectively. The results are shown in Fig. 4.

From Fig. 4, it can be seen that aluminum removal rate increases along with pH value of lixivium. Meanwhile, the RE loss rate also increases. When pH value is 5.0, the aluminum removal rate reaches 94.4 % and RE loss rate is 10.4 %. When pH value exceeds 5.0, the aluminum removal rate barely changes. Clearly, the aluminum

Fig. 4 Effects of ammonia dosage on Al removal rate and RE loss rate

removing process of low-concentration lixivium has a high RE loss rate when using ammonia as pH regulator. Thus, ammonia is not suitable for removing aluminum from lixivium.

3.3 Effects of ammonium bicarbonate on removing aluminum

When NH_4HCO_3 was added into the lixivium, Al^{3+} would be precipitated. It can be described by the following reaction [16]:

$$Al^{3+} + 3NH_4HCO_3 = Al(OH)_3\downarrow + 3CO_2\uparrow + 3NH_4^+ \quad (1)$$

However, there exists side reaction at the same time, which can be described by the following reaction [17]:

$$2RE^{3+} + 6CO_3^{2-} = 2RE_2(CO_3)_3\downarrow + 6CO_2\uparrow + 3H_2O \quad (2)$$
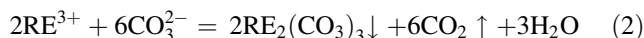
Thus, in the aluminum removing process, the dosage of ammonium bicarbonate should be controlled strictly to avoid the side reaction. The ammonium bicarbonate used

in the experiment was dissolved into deionized water. The concentration of the prepared ammonium bicarbonate solution is 1.83 mol·L^{-1}. Moreover, the pH value of ammonium bicarbonate solution is 8.2. In the experiment, ammonium bicarbonate solution with different dosages was added into the lixivium at a uniform velocity to adjust pH value of the lixivium to 4.4, 4.6, 4.8, 5.0, 5.2, and 5.4, respectively. The results are shown in Fig. 5.

Figure 5 shows that the aluminum removal rate and the RE loss rate increase significantly with the increase of ammonium bicarbonate dosage. When the aluminum removal rate of is 91.3 %, the RE loss rate reaches 20.1 %. The aluminum in the lixivium would exhaust the ammonium bicarbonate, resulting in a change of pH value. Under this condition, side reaction becomes strong to make an increase of RE loss rate [21].

3.4 Effects of sodium acetate on removing aluminum

Sodium acetate solution with concentration of 1.83 mol·L^{-1} (pH value of 8.7) was used to remove aluminum from lixivium. Sodium acetate solution with different dosages was added into lixivium at a uniform velocity to adjust pH value of lixivium to 4.4, 4.6, 4.8, 5.0, 5.2 and 5.4, respectively. The results are shown in Fig. 6.

Figure 6 shows that the aluminum removal rate is very low (<15 %) even when the sodium acetate dosage of at a high level. Clearly, the effect of sodium acetate on removing aluminum from the low-concentration lixivium is very poor. Thus, it is not suitable to use as pH regulator.

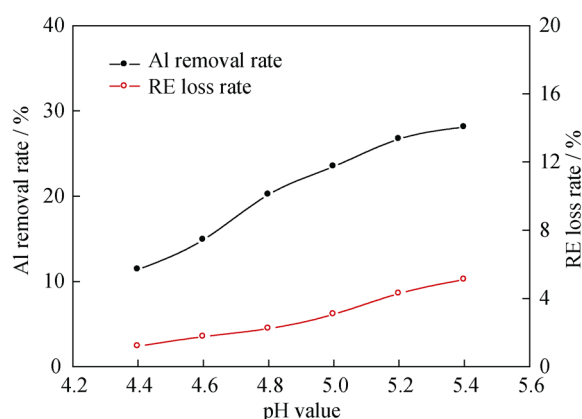### 3.5 Effects of sodium sulfide dosage on removing aluminum

Sodium sulfide solution (pH value of above 12) was used as pH regulator. The results are shown in Fig. 7. When
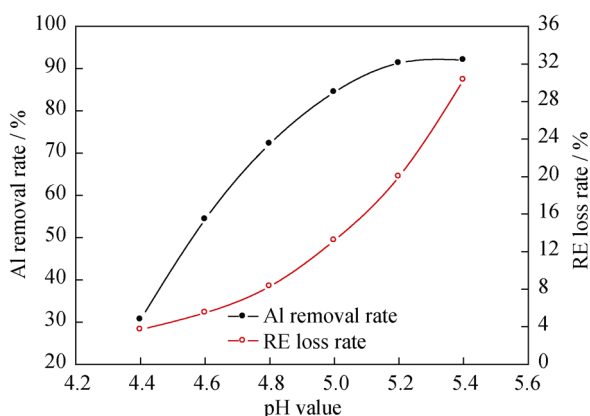
Fig. 5 Effects of ammonium bicarbonate dosage on Al removal rate and RE loss rate
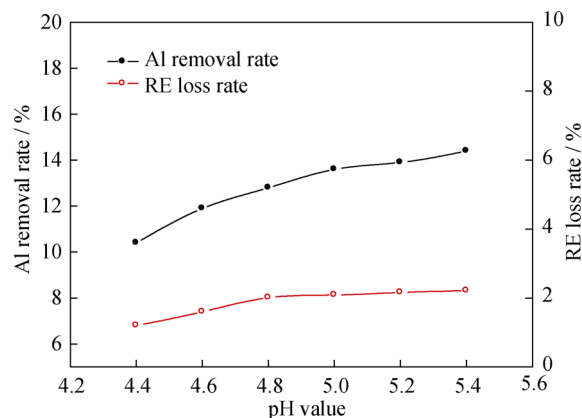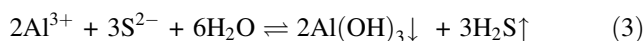

Fig. 6 Effects of sodium acetate dosage on Al removal rate and RE loss rate

Fig. 7 Effects of sodium sulfide dosage on Al removal rate and RE loss rate

sodium sulfide solution was added into lixivium, S^{2-} and Al^{3+} in lixivium have double hydrolysis reaction [16]:

$$2Al^{3+} + 3S^{2-} + 6H_2O \rightleftharpoons 2Al(OH)_3\downarrow + 3H_2S\uparrow \qquad (3)$$

It can be seen from Fig. 7 that the aluminum removal rate is very low when using sodium sulfide as pH regulator, due to that the H$_2$S generated in the reaction would make the precipitated aluminum dissolve again [16]. Thus, the sodium sulfide is not suitable as pH regulator to remove aluminum from low-concentration lixivium.

3.6 Effects of hexamethylenetetramine on removing aluminum

Hexamethylenetetramine solution is alkaline and has a certain buffer action. In this stage, hexamethylenetetramine solution (concentration of 1.43 mol·L^{-1} and pH value of above 12) was used to remove aluminum from low-concentration lixivium. Hexamethylenetetramine with different dosages was added into lixivium at a uniform velocity

to adjust pH value of lixivium to 4.4, 4.6, 4.8, 5.0, 5.2, and 5.4, respectively. The results are shown in Fig. 8.

It can be seen from Fig. 8 that the aluminum removal rate reaches 97.6 % when the pH value of lixivium is 5.0. Under this condition, the RE loss rate is only 4.02 %. Clearly, compared to other pH regulators, hexamethylenetetramine has good effect on removing aluminum from low-concentration lixivium.

The main reason that hexamethylenetetramine has good effect on removing aluminum mostly lies in two aspects. Firstly, hexamethylenetetramine solution has a certain buffer action. With the addition of hexamethylenetetramine, the pH value of lixivium keeps at a stable range. It makes a high aluminum removal rate and a low RE loss. Secondly, compared to other pH regulators, there are not side chemical reactions existing when using hexamethylenetetramine. It effectively reduces the RE loss rate in aluminum removing process.

Obviously, in the four pH regulators (ammonia, ammonium bicarbonate, hexamethylenetetramine, sodium acetate and sodium sulfide), hexamethylenetetramine is the optimum choice for the removing of aluminum from low-concentration RE lixivium.

3.7 Effects of aluminum on RE precipitation process

The existence of aluminum in lixivium has adverse effects on precipitating RE from lixivium. These adverse effects are mainly caused by the co-precipitation of aluminum ions with RE ions. Firstly, the purity of RE product will decline. And secondly, the precipitated aluminum is colloid, which would wrap on the surface of RE precipitation [21–23]. In this case, the precipitated RE forms flocculent RE precipitation rather than crystalline RE carbonates. Compared to crystalline RE carbonates, the flocculent RE precipitation
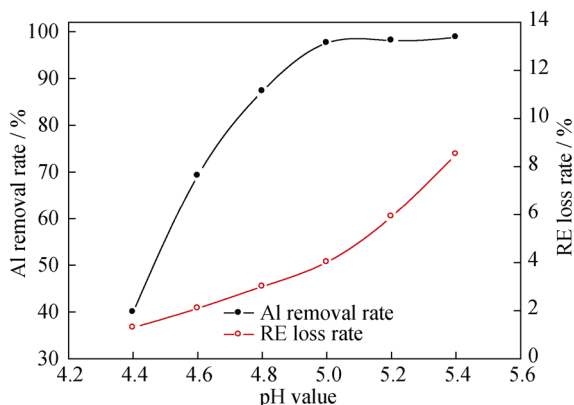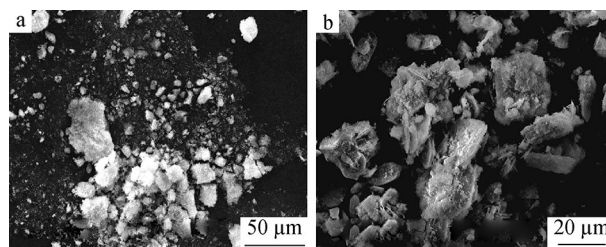
Fig. 9 SEM images of RE product, **a** prepared from purified lixivium and **b** prepared from unpurified lixivium

has a particular larger volume, which is difficult to filter [24].

Figure 9a shows SEM image of final RE products precipitated from unpurified lixivium (aluminum has not been removed) [25]. It can be seen that the shape of the RE product from unpurified lixivium is very fuzzy. The RE product is amorphous solids, which are difficult to filter. Thus, it confirms the adverse effect of aluminum ions on the RE precipitation process [26]. Figure 9b shows SEM image of final RE products precipitated from lixivium, which contains little aluminum (most of aluminum has been removed by hexamethylenetetramine). It shows that the RE product is crystal solid, which has large particle size and is easy to filter. It again proves that hexamethylenetetramine has little adverse effect on the precipitation process of RE.

4 Conclusion

The existence of aluminum ions in the lixivium has a significant adverse effect on rare earth precipitation process. The aluminum in the lixivium would be co-precipitated with the rare earth precipitation, resulting in the decrease of the purity of the final rare earth products. Beside, its existence in the lixivium makes the precipitation form flocculent rare earth carbonates (not beneficial for further processing) rather than crystalline precipitation.

The effect of sodium acetate and sodium sulfide on removing aluminum from the low-concentration rare earth lixivium is very bad. Large amount of rare earth is loss when they were used as pH regulator to remove aluminum. In contrast, hexamethylenetetramine shows a significantly better performance on removing aluminum. When using hexamethylenetetramine as pH regulator, the removal rate of aluminum and the loss rate of rare earth reach 97.6 % and 4.02 %, respectively. Hexamethylenetetramine is the optimum choice for removing aluminum from low-concentration rare earth lixivium.

Fig. 8 Effects of hexamethylenetetramine dosage on Al removal rate and RE loss rate

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