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One step purification of impurities in the leachate of weathered crust elution-deposited rare earth ores

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Abstract: It is necessary to control and reduce the high content of Al^{3+}, Cu^{2+} and Pb^{2+} ions in the leachate of weathered crust elution-deposited rare earth ore to facilitate the rare earth recovery and the quality of rare earth products. Neither NH_4HCO_3 nor Na_2S are suitable for removal of all impurity ions and meanwhile maintain high rare earth recovery. Conventionally, NH_4HCO_3 is firstly adopted to remove Al^{3+}, and then Cu^{2+} and Pb^{2+} are removed by using Na_2S. This two steps purification process is quite long and results in lots of complication in operation. In this paper, a one-step purification by using the compound of NH_4HCO_3 and Na_2S was proposed to remove Al^{3+}, Cu^{2+} and Pb^{2+}. The results showed that after purification 89% Cu, 92% Pb and 74% Al were removed from the leachate solution by using 0.1 M compound of NH_4HCO_3/Na_2S, while maintaining 89% rare earth. The optimal purification parameters were: volume ratio of NH_4HCO_3 to Na_2S of 9:1, volume ratio of compound to leachate of 0.05:1, precipitation time of 30 min.

Keywords: *leachate, weathered crust, rare earth ore, leachate purification, precipitation*

Introduction

The weathered crust elution-deposited rare earth ore rich in medium and heavy rare earth (RE) is the China unique mineral resource, which is distributed in southern China, such as Jiangxi, Fujian, Hunan, Guangdong and Guangxi (Chi and Tian, 2008; He et al., 2016a). The weathered crust elution-deposited rare earth ore is composed of clay minerals that absorb rare earth ions (Chi et al., 2005). According to the property of the rare earth mainly as an ion-exchange phase in the ore, many researchers have suggested leaching of RE with an electrolyte solution (He et al., 2016b; Huang et al., 2005; Xiao et al., 2015a; Zhang et al., 2016; Luo et al., 2015a; Moldoveanu and Papangelakis, 2016). The challenge of the proposed electrolyte solution leaching process is that the leachate from the weathered crust elution-deposited rare earth ore contains high levels of impurity ions, and subsequently has a low concentration of RE

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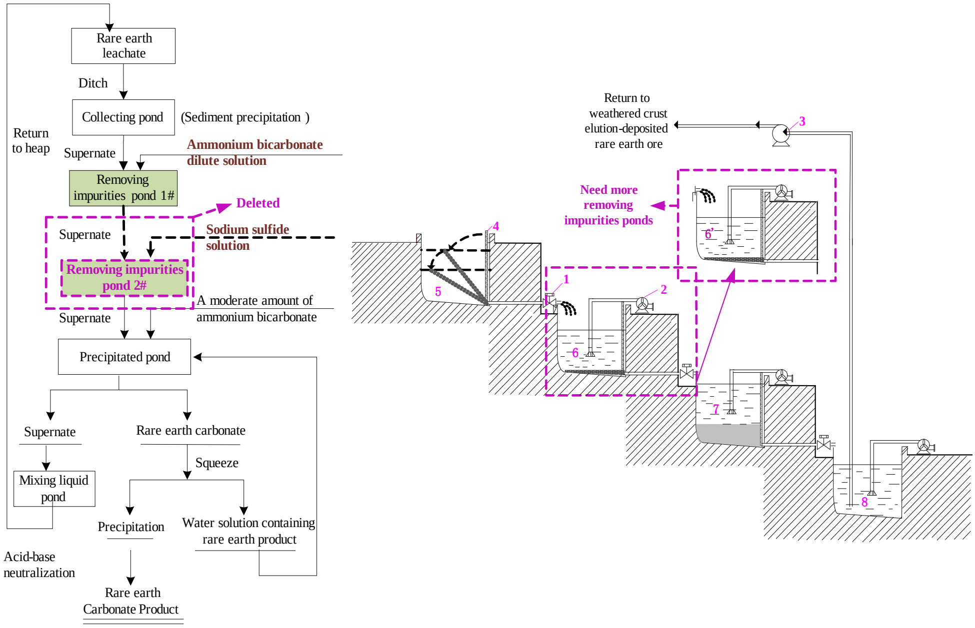
(Xiao et al., 2015b; Luo et al., 2015b). The typical impurity ions in the leachate are Al^{3+}, Cu^{2+} and Pb^{2+}, which participate in the leaching process (Zuo et al., 2007). They must be removed, otherwise it affects the quality of rare earth precipitation products, greatly increasing the consumption of oxalic acid, and even difficult to form rare earth carbonate crystals.

NH_4HCO_3 as a neutralizing reagent can be used to remove impurities from the RE leachate. The Al^{3+} can be hydrolyzed and subsequently precipitated as hydroxide, while rare earth ions do not precipitate at the appropriate pH. However, Pb^{2+} is not suitable to be removed by NH_4HCO_3 as it has the same precipitation pH as RE^{3+}(Chi and Tian, 2008). For Cu^{2+} and Pb^{2+} removal, there are a number of conventional methods such as chemical precipitation (Bozecka et al., 2016), ion exchange (Rao et al., 2010) and adsorption by active carbon (Machida et al., 2012) which can be used. Among these methods, chemical precipitation is widespread for RE leachate purification due to the equipment conveniences and the low cost of operation. Al^{3+} in the RE leachate solution is first removed by either NH_4HCO_3 or other aluminum removal agents, and then Cu^{2+} and Pb^{2+} are precipitated by sulfite. Either a two-step or multi-step purification is needed resulting in a longer purification procedure and a complicated operation.



(a) (b)

Fig. 1. Comparison of proposed one-step purification to conventional two-step procedure, (a) flowsheet of leaching solution treatment; (b) profile map of setting ponds (1 – ball valve, 2 – blower, 3 – pump, 4 – plastic tubing, 5 – collecting pond, 6 – removing impurities pond 1#, 6’ – removing impurities pond 2#, 7 – precipitation pond, 8 – mixing liquid pond)

One-step purification by using the compound of NH_4HCO_3 and Na_2S is proposed to remove the impurity ions of Al^{3+}, Cu^{2+} and Pb^{2+}. The proposed flowsheet for the RE leachate purification is shown in Fig. 1 and compared to the conventional two-step purification flowsheet. Figure 1 shows that when the proposed compound of NH_4HCO_3 and Na_2S is used as a precipitator, the impurities pond 2# can be removed. The conventional two-step or multi-step purification is simplified to a one-step, which saves a row of precipitation ponds. For a further investigation on purification effects, the precipitation time, volume ratio, slurry pH and volume ration of compound were discussed towards to maintain RE recovery and increase Al^{3+}, Cu^{2+} and Pb^{2+} removal rates.

Experimental procedure

Materials

All reagent grade chemicals in this study were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Reagent grade HCl and ammonia were used as pH modifiers. The deionized water was produced by a water purification system. A weathered crust elution-deposited rare earth ore from Dingnan City, Jiangxi Province, China, was leached by 0.1 M NH_4Cl solutions to collect the leachate for the removing impurities experiments, where the contents of RE, Al^{3+}, Cu^{2+} and Pb^{2+} in RE leachate were 0.722 g/dm^3, 0.159 g/dm^3, 0.46 mg/dm^3 and 4.24 mg/dm^3, respectively.

Removing impurities experiment

A 100 cm^3 RE leachate was mixed with different concentrations and volumes of NH_4HCO_3 or/and Na_2S for each measurement. After standing for a certain precipitation time, the solutions were filtered, and then analyzed to calculate the recovery of RE, the removal rates of Al^{3+}, Cu^{2+} and Pb^{2+}.

Analytical methods

The total content of RE in solutions was analyzed by EDTA titration, and the Al^{3+} content in solutions was analyzed by EDTA inverse titration. The detail description can be found elsewhere (He et al., 2015, 2016a, b). The contents of Cu^{2+} and Pb^{2+} in solutions were tested by an atomic absorption spectrophotometer (AA6300; Shimadzu, Japan). Then, the RE recovery and the removal rates of Al^{3+}, Cu^{2+}, and Pb^{2+} for each purification experiment were calculated as follows:

$$R_{RE} = \frac{C'_{RE}}{C_{RE}} \cdot 100\% \tag{1}$$

$$R_{impurity\ ions} = \frac{C - C'}{C} \cdot 100\% \tag{2}$$

where, the R_{RE} is the RE recovery, the $R_{impurity\ ions}$ is the removal rate of impurity ions, C'_{RE} and C' are the RE and impurity ions contents after purification, respectively, C_{RE} and C are the RE and impurity ions content of leachate, respectively.

Results and discussion

Removal of impurities from rare earth leachate by NH_4HCO_3

Effect of precipitation time

NH_4HCO_3 as a typical weak acid and weak base salt is easy to decompose in the aqueous solution. The hydroxide ion by hydrolysis can remove the impurity ions from the RE leachate through the precipitation reaction (Iskrenova and Patnaik, 2016). The NH_4HCO_3 solutions with different concentrations were discussed under different volume ratios and solution pHs in order to know its removal characteristics.

The precipitation time of NH_4HCO_3, Na_2S and their compound are determined from Figure 2. Figure 2 shows that the RE recovery and the removal rates of impurity ions increase with the increasing of precipitation time, and all of them are approaching to the equilibrium point at around 30 min. Therefore, the precipitation time is determined as 30 min for the following experiments.

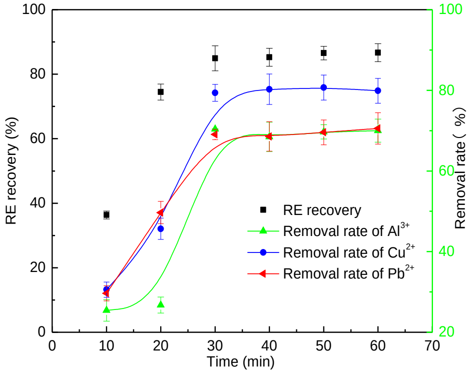


Fig. 2. Effect of precipitation time on the RE recovery and removal rates of Al^{3+}, Cu^{2+} and Pb^{2+} (NH_4HCO_3 concentration: 7.9%; NH_4HCO_3/leachate volume ratio: 0.05:1; pH = 4.8; room temperature)

Effect of NH_4HCO_3/leachate volume ratio

The 7.9% of NH_4HCO_3 solutions were mixed with RE leachates at pH 4.8 at different volume ratios (NH_4HCO_3 : leachate), 0.02:1, 0.03:1, 0.04:1, 0.05:1, 0.06:1, 0.08:1, 0.1:1 for 30 min, and then the solutions were filtered and analyzed. The results are shown in Fig. 3. From Figure 3, the RE recovery decreases with the increase of NH_4HCO_3 consumption, but the removal rates of impurity ions increase, suggesting that both the RE ions and the impurity ions can be precipitated by the NH_4HCO_3 solution. At the volume ratio of 0.05:1, the removal rates of Al^{3+}, Pb^{2+} and Cu^{2+} reach relative high values, 70, 69 and 79%, respectively. The RE recovery is about 84%. Thus, 0.05:1 was chosen as a suitable volume ratio in the purification experiments by NH_4HCO_3.

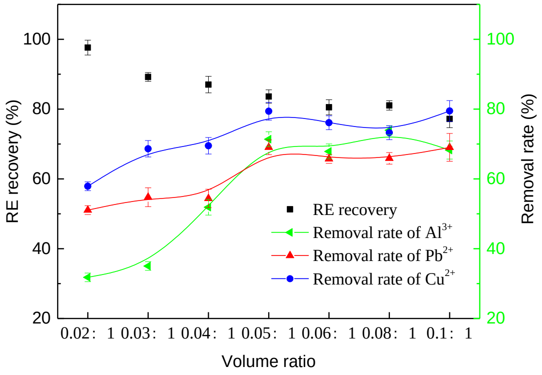


Fig. 3. Effect of NH_4HCO_3/leachate volume ratio on RE recovery and removal rates of Al^{3+}, Cu^{2+} and Pb^{2+} (NH_4HCO_3 concentration:7.9%; pH = 4.8; precipitation time: 30 min; room temperature)

Effect of NH_4HCO_3 concentration

At a volume ratio of 0.05:1 and solution pH of 4.8, NH_4HCO_3 solutions with different mass concentrations, that is 3.5, 4.6, 5.58, 6.8, 7.9, 8.7 and 9.8%, were applied to remove the impurity ions from the RE leachate. The RE recovery and the removal rates of Al^{3+}, Pb^{2+} and Cu^{2+} are shown in Figure 4.

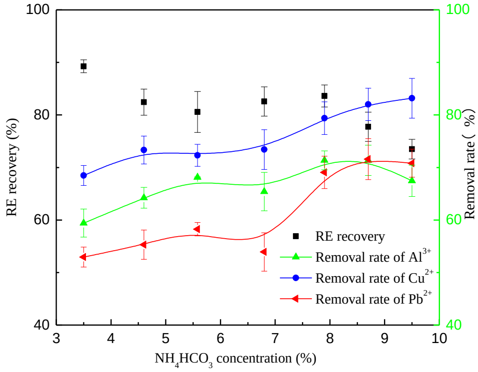


Fig. 4. Effect of NH_4HCO_3 concentration on RE recovery and removal rates of Al^{3+}, Cu^{2+} and Pb^{2+} (NH_4HCO_3/leachate volume ratio :0.05:1; pH = 4.8; precipitation time: 30 min; room temperature)

The RE recovery decreases with the NH_4HCO_3 concentration increase (Fig. 4). The removal rates of Pb^{2+} and Cu^{2+} increase with the NH_4HCO_3 concentration increase, and gradually tend to be steady when the NH_4HCO_3 concentration is higher than 7.9%. The removal rate of Al^{3+} is up to the highest value at the NH_4HCO_3 concentration of 7.9%, and then decreases with the NH_4HCO_3 concentration increase. Aluminum in the

RE leachate exists as various forms with the pH change, such as Al^{3+}, $Al(OH)_3$, AlO_2^- and others. The precipitate of $Al(OH)_3$ is a typical amphoteric compound, which dissolves in the alkaline environment resulting from the high NH_4HCO_3 concentration. The suitable NH_4HCO_3 concentration is thus 7.9% for the purification experiment by NH_4HCO_3.

Effect of solution pH

Since the strong alkalis condition is adverse to the RE recovery (Yu et al., 1993; Zhang et al., 1996), the effects of solution pH in the range from 4.4 to 6.5 are discussed and shown in Fig. 5. With increasing of pH, the RE recovery decreases due to precipitation of RE ions in the weak alkaline environment (Chi and Tian, 2008). The removal rates of Pb^{2+} and Cu^{2+} increase with the pH increase, and the Al^{3+} reaches the highest value at pH 4.8. The suitable pH is thus determined as 4.8 for NH_4HCO_3 as precipitator.

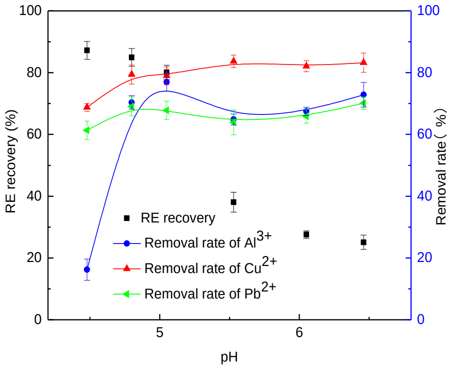


Fig. 5. Effect of solution pH on RE recovery and removal rates of Al^{3+}, Cu^{2+} and Pb^{2+} (NH_4HCO_3/leachate volume ratio :0.05:1; NH_4HCO_3 concentration: 7.9%; precipitation time: 30 min; room temperature)

The optimum technological conditions for removing impurity ions from RE leachate by NH_4HCO_3 are obtained as 0.05:1 of volume ratio, 7.9% of NH_4HCO_3 concentration and 4.8 of pH. About 70% of Al^{3+}, 79% Cu^{2+}, 69% Pb^{2+} in RE leachate are removed and 84% RE are kept. Here, the removal rates of Cu^{2+} and Pb^{2+}, 79% and 69%, are imperfect for the following rare earth product industrial production. A better precipitator is thus still needed to find.

Removal of impurities from rare earth leachate by Na_2S

The purification results with NH_4HCO_3 as the precipitator indicate the importance of solution pH over the concentration and volume ratio. For a better comparison of Na_2S to NH_4HCO_3, 0.1 M Na_2S solutions with the same concentration to NH_4HCO_3 were mixed with 100 cm^3 RE leachates at the same volume ratio of 0.05:1, and then the solution pHs were adjusted to 3.94, 4.57, 4.91, 5.36 and 5.81, respectively. After precipitation and filtration, the RE recovery and the removal rates of Al^{3+}, Pb^{2+} and Cu^{2+} were analyzed and the results are shown in Fig. 6. From Figure 6, the high recovery of RE has a little change among the tested pH range suggesting that no rare earth sulfide or hydroxide is generated, since the precipitation pH of rare earth hydroxide is around 6.0-8.0 (Chi and Tian, 2008). For the Pb^{2+} and Cu^{2+}, a similar variation tendency like the RE recovery is investigated and almost all of Cu^{2+} are removed, indicating that Pb^{2+} and Cu^{2+} impurity ions are precipitated by forming PbS and CuS. Na_2S reacts to Al^{3+} as follows:

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

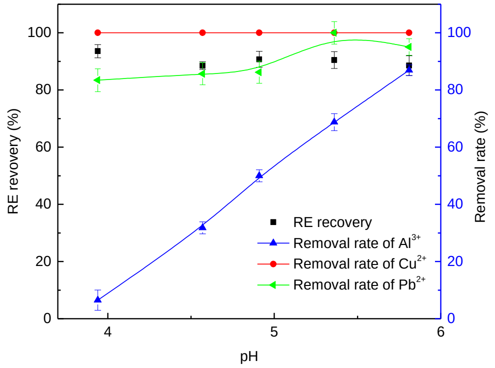


Fig. 6. Effect of Na_2S on RE recovery and removal rates of Al^{3+}, Cu^{2+} and Pb^{2+} as a function of pH (Na_2S /leachate volume ratio :0.05:1; Na_2S concentration: 0.1 M; precipitation time: 30 min; room temperature)

The S^{2-} content in the solution decreases in the weak acid environment or in the weakly acidic RE leachate due to the generation of H_2S. The removal rate of Al^{3+} is thus very low among pH 3.94-5, and then increases with the pH increase (Fig. 6). The results in Fig. 6 suggest that Na_2S is a good precipitator to remove Pb^{2+} and Cu^{2+} from the RE leachate and while keeps a high RE recovery, especially at pH higher than 5.5. However, the potential H_2S by-product is a toxic chemical and the presence of S^{2-} in the solutions is disadvantageous to production of rare earth carbonate in the following RE industrial production. Thus, Na_2S as the precipitator is imperfect to remove impurity ions from the RE leachate.

Impurity ions behavior of Al^{3+}, Cu^{2+} and Pb^{2+} with NH_4HCO_3 and Na_2S

The principle of removing impurities by NH_4HCO_3 is that the part of impurity ions is hydrolyzed, and then precipitated as hydroxide while rare earth ions are not precipitated. Sodium sulfide is worked through the black precipitate formation of heavy metal sulfides. The possible reactions are as follows:

$$Al^{3+} + 3OH^{-} = Al(OH)_3\downarrow \tag{4}$$

$$Cu^{2+} + 2OH^{-} = Cu(OH)_2\downarrow \tag{5}$$

$$Pb^{2+} + 2OH^{-} = Pb(OH)_2\downarrow \tag{6}$$

$$Cu^{2+} + S^{2-} = CuS\downarrow \tag{7}$$

$$Pb^{2+} + S^{2-} = PbS\downarrow. \tag{8}$$

The solubility product constants K_{sp} of these precipitates are shown in Table 1.

Table 1. K_{sp} of metal precipitates formed with impurity ions

Elements	Precipitate	K_{sp}
RE^{3+}	$RE(OH)_3$	3.0×10^{-24}
Al^{3+}	$Al(OH)_3$	1.30×10^{-33}
Cu^{2+}	$Cu(OH)_2$	2.20×10^{-20}
	CuS	6.00×10^{-26}
Pb^{2+}	$Pb(OH)_2$	1.20×10^{-15}
	PbS	9.04×10^{-29}

For the hydroxide precipitates

$$M^{n+} + nOH^{-} = M(OH)_n\downarrow \tag{9}$$

K_{sp} is described as:

$$K_{sp} = [Mn^{+}][OH^{-}]^{n} \tag{10}$$

$$H^{+} + OH^{-} \leftrightarrow H_2O \tag{11}$$

$$K_w = [H^{+}][OH^{-}] = 10^{-14}. \tag{12}$$

By taking minus logarithm of both sides, the relationships between pM (RE^{3+}, Al^{3+}, Cu^{2+}, Pb^{2+}) and pH are obtained as follows:

$$pM_{RE^{3+}} = 3pH - 18.48 \tag{13}$$

$$pM_{Al^{3+}} = 3pH - 9.11 \tag{14}$$

$$pM_{Cu^{2+}} = 2pH - 22.34 \tag{15}$$

$$pM_{Pb^{2+}} = 2pH - 27.08. \tag{16}$$

For the sulfide precipitates, the relationships between pM (Cu^{2+}, Pb^{2+}) and pH are also obtained by the same method as follows:

$$pM_{Cu^{2+}} = 2pH + 3.30 \tag{17}$$

$$pM_{Pb^{2+}} = 2pH + 6.12. \tag{18}$$

Figure 7 is the pM-pH of NH_4HCO_3 and Na_2S system obtained from Eqs. 13-18, where Al^{3+} exists on the left of blue line and $Al(OH)_3$ is on the other side. The RE^{3+} and $RE(OH)_3$ are on the left and right of black line, respectively. The precipitating pH of $Al(OH)_3$ is lower than that of $RE(OH)_3$, suggesting that most of $Al(OH)_3$ can be precipitated while little RE precipitate is formed, especially at pH 5 (Chi and Tian, 2008). Therefore, Al^{3+} can be removed by the NH_4HCO_3. However, it is not fit for Cu^{2+} and Pb^{2+} due to the higher precipitating pH of $Cu(OH)_2$ and $Pb(OH)_3$ than $RE(OH)_3$. Since RE ions do not react with S^{2-} directly to form the sulfide precipitate, sodium sulfide can be adopted to remove the heavy metal ions in the RE leachate. Figure 7 shows that purple (PbS) and red (CuS) lines are upper than the black line ($RE(OH)_3$), indicating an efficient removing way of Cu^{2+} and Pb^{2+} by sulfide precipitation method.

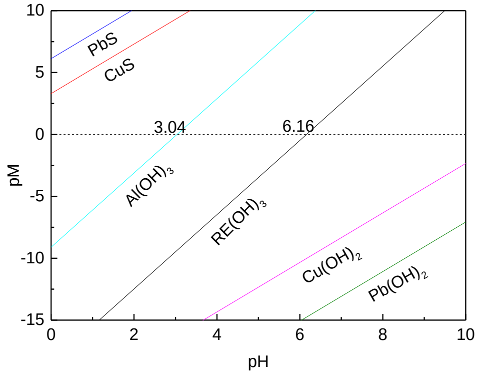


Fig. 7. pM-pH diagram of Al^{3+}, Cu^{2+} and Pb^{2+} in NH_4HCO_3 and Na_2S system

One-step purification of impurities from the rare earth leachate by the compound of NH_4HCO_3 and Na_2S

According to the discussion of impurity ions behavior and the above experiment results, it is found that NH_4HCO_3 is beneficial to Al^{3+} removal, but imperfect to remove Cu^{2+} and Pb^{2+} than Na_2S. Furthermore, NH_4HCO_3 has a less bad influence than Na_2S on the following RE industrial production, and is more environmentally friendly. The compound of NH_4HCO_3 and Na_2S is thus proposed to remove impurity ions from the RE leachate. Different compounds of NH_4HCO_3 and Na_2S with 0.1 M concentration were prepared at the volume ratio of 5:5, 6:4, 7:3, 8:2 and 9:1 for the purification experiments. The effects of different compounds among pH range from 3.0-6.5 are shown in Fig. 8.

It is interesting to find that the RE recovery decreases with the increasing of pH, and decrease to a lower value at pH higher than 5 among all figures, but it does not decrease with the Na_2S dosage increase, which can be attributed to the generation of RE hydroxide and/or carbonate. In Figure 8(a) and 8(b), the removal rate of Al^{3+} and the RE recovery are very low, although the removal rates of Cu^{2+} and Pb^{2+} are very high, indicating an imperfect purification effect of the NH_4HCO_3 and Na_2S compound at volume ratio of 5:5 and 6:4. From Figure 8(c), the removal rate of Al^{3+} is lower than 60% among the tested pH range, although it increases with the increasing of NH_4HCO_3 consumption compared to Fig. 8(b), suggesting the compound of NH_4HCO_3:Na_2S = 7:3 is also unsuitable to remove impurity ions. For the

NH_4HCO_3:Na_2S = 8:2 in Fig. 8(d), the removal rates of Cu^{2+} , Pb^{2+} and Al^{3+} increase with the increasing pH. At pH about 6.0, the removal rate of Al^{3+} is up to 70%, the Cu^{2+} and Pb^{2+} are higher than 86%, but the RE recovery is lower than 65%. A lot of rare earth resources are lost indicating that the NH_4HCO_3:Na_2S = 8:2 is also unsuitable to remove impurity ions from the RE leachate.

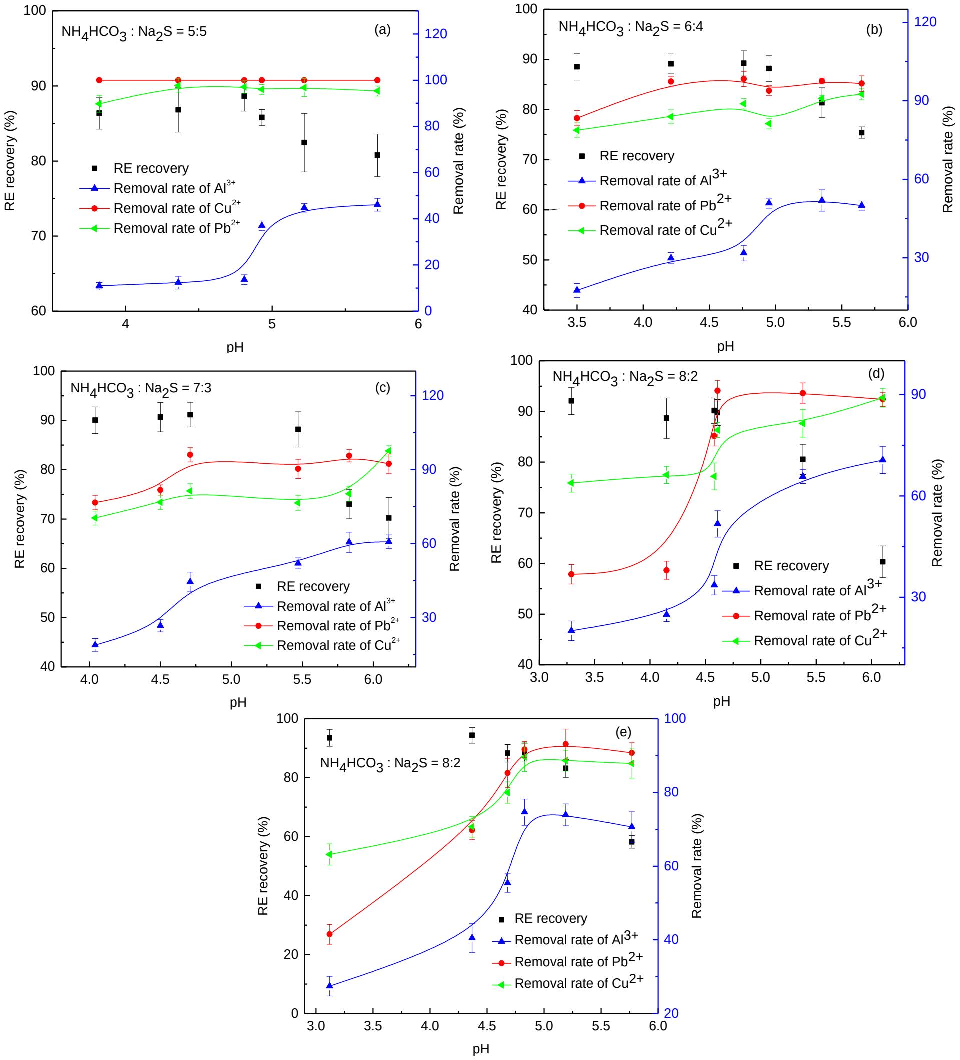


Fig. 8. RE recovery and removal rates of Al^{3+}, Cu^{2+} and Pb^{2+} as a function of pH (compound/leachate volume ratio of 0.05:1; compound concentration 0.1 M; precipitation time 30 min; room temperature); (a) NH_4HCO_3:Na_2S volume ratio of 5:5; (b) NH_4HCO_3:Na_2S volume ratio of 6:4; (c) NH_4HCO_3:Na_2S volume ratio of 7:3; (d) NH_4HCO_3:Na_2S volume ratio of 8:2; (e) NH_4HCO_3:Na_2S volume ratio of 9:1

Figure 8(e) shows that the removal rates of Cu^{2+}, Pb^{2+} and Al^{3+} increase with the increasing pH at the volume ratio of NH_4HCO_3:Na_2S = 9:1. The RE recovery decreases with the pH increase. At the pH around 4.8-5.1, the removal rates of Cu^{2+}, Pb^{2+} and Al^{3+} reach about 89, 92 and 74%, respectively, and the RE recovery is about 89%, indicating that most rare earth resources is kept in the leachate for the following rare earth production and the impurity ions of Cu^{2+}, Pb^{2+} and Al^{3+} are removed. Furthermore, the pH of the compound of NH_4HCO_3 and Na_2S at volume ratio of 9:1 is around 4.9, which is consistent with the optimum pH in the purification process, suggesting an easier and more economic rare earth production without pH modifier.

Conclusions

The results presented in this study showed the single NH_4HCO_3 as precipitator was not effective enough to remove impurity ions especially Cu^{2+} and Pb^{2+} from RE leachate, and Na_2S as the precipitator was beneficial to the precipitation of Cu^{2+} and Pb^{2+}, but fail to precipitate Al^{3+}. For a better impurity purification, the compound of NH_4HCO_3:Na_2S was proposed based on the discussion of impurity ions behavior, which simplified the conventional two-step or multi-step purification to a one-step procedure. The optimum technological conditions for the system were obtained: compound concentration 0.1 M, NH_4HCO_3:Na_2S 9:1, compound/leachate volume ratio 0.05:1, precipitation time 30 min and the solution pH around 4.9 without any pH modifier. A purified RE leachate with the removal rates of Cu^{2+}, Pb^{2+} and Al^{3+} reaching about 89, 92, 74%, respectively, and the RE recovery being about 89% were obtained, which was suitable to the following rare earth production.

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