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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  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  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  $\text{NH}_4\text{HCO}_3$  nor  $\text{Na}_2\text{S}$  are suitable for removal of all impurity ions and meanwhile maintain high rare earth recovery. Conventionally,  $\text{NH}_4\text{HCO}_3$  is firstly adopted to remove  $\text{Al}^{3+}$ , and then  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  are removed by using  $\text{Na}_2\text{S}$ . 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  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  was proposed to remove  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ . 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  $\text{NH}_4\text{HCO}_3/\text{Na}_2\text{S}$ , while maintaining 89% rare earth. The optimal purification parameters were: volume ratio of  $\text{NH}_4\text{HCO}_3$  to  $\text{Na}_2\text{S}$  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

(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.

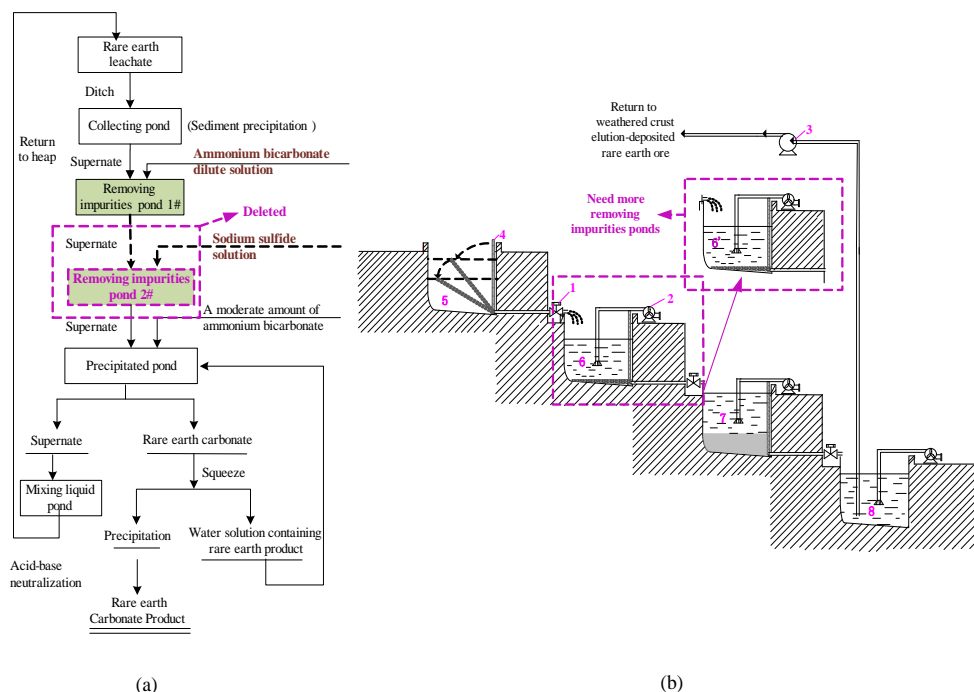


Fig. 1. Comparison of proposed one-step purification to conventional two-step procedure, (a) flowsheet of leaching solution treatment; (b) profile map of setting ponds (1 – ball valve, 2 – blower, 3 – pump, 4 – plastic tubing, 5 – collecting pond, 6 – removing impurities pond 1#, 6’ – removing impurities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

One-step purification by using the compound of  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  is proposed to remove the impurity ions of  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ . 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  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  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  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  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  $\text{NH}_4\text{Cl}$  solutions to collect the leachate for the removing impurities experiments, where the contents of RE,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  in RE leachate were  $0.722 \text{ g/dm}^3$ ,  $0.159 \text{ g/dm}^3$ ,  $0.46 \text{ mg/dm}^3$  and  $4.24 \text{ mg/dm}^3$ , respectively.

### Removing impurities experiment

A  $100 \text{ cm}^3$  RE leachate was mixed with different concentrations and volumes of  $\text{NH}_4\text{HCO}_3$  or/and  $\text{Na}_2\text{S}$  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  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ .

### Analytical methods

The total content of RE in solutions was analyzed by EDTA titration, and the  $\text{Al}^{3+}$  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  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  in solutions were tested by an atomic absorption spectrophotometer (AA6300; Shimadzu, Japan). Then, the RE recovery and the removal rates of  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$  for each purification experiment were calculated as follows:

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

$$R_{\text{impurity ions}} = \frac{C - C'}{C} \cdot 100\% \quad (2)$$

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.

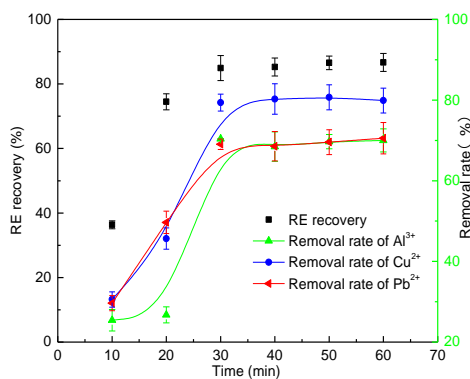


Fig. 2. Effect of precipitation time on the RE recovery and removal rates of  $Al^{3+}$ ,  $Cu^{2+}$  and  $Pb^{2+}$  ( $NH_4HCO_3$  concentration: 7.9%;  $NH_4HCO_3$ /leachate volume ratio: 0.05:1; pH = 4.8; room temperature)

#### 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  $\text{NH}_4\text{HCO}_3$ .

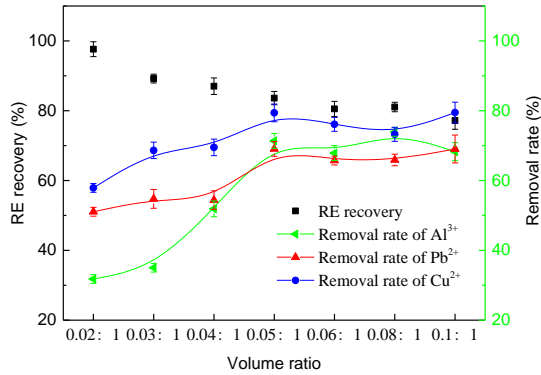


Fig. 3. Effect of  $\text{NH}_4\text{HCO}_3$ /leachate volume ratio on RE recovery and removal rates of  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ( $\text{NH}_4\text{HCO}_3$  concentration: 7.9%; pH = 4.8; precipitation time: 30 min; room temperature)

#### Effect of $\text{NH}_4\text{HCO}_3$ concentration

At a volume ratio of 0.05:1 and solution pH of 4.8,  $\text{NH}_4\text{HCO}_3$  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  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  are shown in Figure 4.

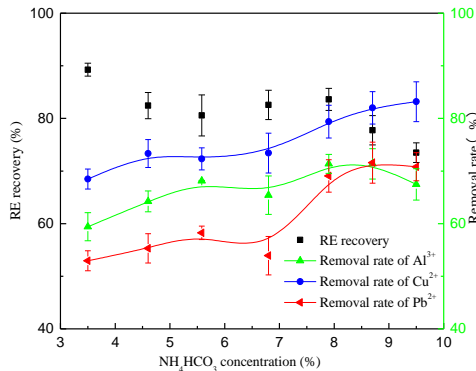


Fig. 4. Effect of  $\text{NH}_4\text{HCO}_3$  concentration on RE recovery and removal rates of  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ( $\text{NH}_4\text{HCO}_3$ /leachate volume ratio :0.05:1; pH = 4.8; precipitation time: 30 min; room temperature)

The RE recovery decreases with the  $\text{NH}_4\text{HCO}_3$  concentration increase (Fig. 4). The removal rates of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  increase with the  $\text{NH}_4\text{HCO}_3$  concentration increase, and gradually tend to be steady when the  $\text{NH}_4\text{HCO}_3$  concentration is higher than 7.9%. The removal rate of  $\text{Al}^{3+}$  is up to the highest value at the  $\text{NH}_4\text{HCO}_3$  concentration of 7.9%, and then decreases with the  $\text{NH}_4\text{HCO}_3$  concentration increase. Aluminum in the

RE leachate exists as various forms with the pH change, such as  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{AlO}_2^-$  and others. The precipitate of  $\text{Al}(\text{OH})_3$  is a typical amphoteric compound, which dissolves in the alkaline environment resulting from the high  $\text{NH}_4\text{HCO}_3$  concentration. The suitable  $\text{NH}_4\text{HCO}_3$  concentration is thus 7.9% for the purification experiment by  $\text{NH}_4\text{HCO}_3$ .

### 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  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  increase with the pH increase, and the  $\text{Al}^{3+}$  reaches the highest value at pH 4.8. The suitable pH is thus determined as 4.8 for  $\text{NH}_4\text{HCO}_3$  as precipitator.

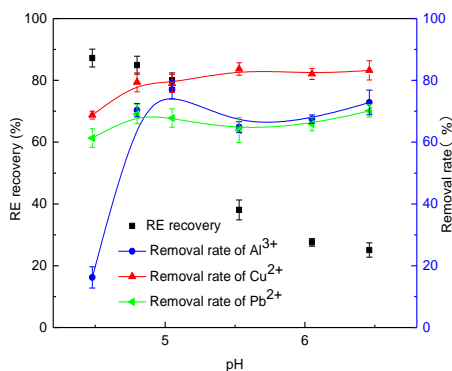


Fig. 5. Effect of solution pH on RE recovery and removal rates of  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ( $\text{NH}_4\text{HCO}_3/\text{leachate}$  volume ratio :0.05:1;  $\text{NH}_4\text{HCO}_3$  concentration: 7.9%; precipitation time: 30 min; room temperature)

The optimum technological conditions for removing impurity ions from RE leachate by  $\text{NH}_4\text{HCO}_3$  are obtained as 0.05:1 of volume ratio, 7.9% of  $\text{NH}_4\text{HCO}_3$  concentration and 4.8 of pH. About 70% of  $\text{Al}^{3+}$ , 79%  $\text{Cu}^{2+}$ , 69%  $\text{Pb}^{2+}$  in RE leachate are removed and 84% RE are kept. Here, the removal rates of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , 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 $\text{Na}_2\text{S}$

The purification results with  $\text{NH}_4\text{HCO}_3$  as the precipitator indicate the importance of solution pH over the concentration and volume ratio. For a better comparison of  $\text{Na}_2\text{S}$  to  $\text{NH}_4\text{HCO}_3$ , 0.1 M  $\text{Na}_2\text{S}$  solutions with the same concentration to  $\text{NH}_4\text{HCO}_3$  were mixed with 100  $\text{cm}^3$  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  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  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  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ , a similar variation tendency like the RE recovery is investigated and almost all of  $\text{Cu}^{2+}$  are removed, indicating that  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  impurity ions are precipitated by forming  $\text{PbS}$  and  $\text{CuS}$ .  $\text{Na}_2\text{S}$  reacts to  $\text{Al}^{3+}$  as follows:

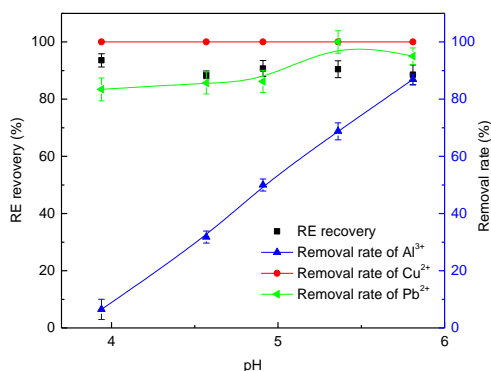
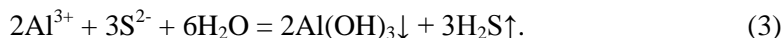


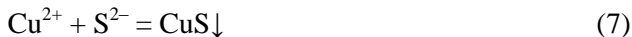
Fig. 6. Effect of  $\text{Na}_2\text{S}$  on RE recovery and removal rates of  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  as a function of pH ( $\text{Na}_2\text{S}$  /leachate volume ratio :0.05:1;  $\text{Na}_2\text{S}$  concentration: 0.1 M; precipitation time: 30 min; room temperature)

The  $\text{S}^{2-}$  content in the solution decreases in the weak acid environment or in the weakly acidic RE leachate due to the generation of  $\text{H}_2\text{S}$ . The removal rate of  $\text{Al}^{3+}$  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  $\text{Na}_2\text{S}$  is a good precipitator to remove  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  from the RE leachate and while keeps a high RE recovery, especially at pH higher than 5.5. However, the potential  $\text{H}_2\text{S}$  by-product is a toxic chemical and the presence of  $\text{S}^{2-}$  in the solutions is disadvantageous to production of rare earth carbonate in the following RE industrial production. Thus,  $\text{Na}_2\text{S}$  as the precipitator is imperfect to remove impurity ions from the RE leachate.

### Impurity ions behavior of $\text{Al}^{3+}$ , $\text{Cu}^{2+}$ and $\text{Pb}^{2+}$ with $\text{NH}_4\text{HCO}_3$ and $\text{Na}_2\text{S}$

The principle of removing impurities by  $\text{NH}_4\text{HCO}_3$  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:





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

For the hydroxide precipitates



$K_{sp}$  is described as:

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



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

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

$$\text{pM}_{\text{RE}^{3+}} = 3\text{pH} - 18.48 \tag{13}$$

$$\text{pM}_{\text{Al}^{3+}} = 3\text{pH} - 9.11 \tag{14}$$

$$\text{pM}_{\text{Cu}^{2+}} = 2\text{pH} - 22.34 \tag{15}$$

$$\text{pM}_{\text{Pb}^{2+}} = 2\text{pH} - 27.08. \tag{16}$$

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

$$\text{pM}_{\text{Cu}^{2+}} = 2\text{pH} + 3.30 \tag{17}$$

$$\text{pM}_{\text{Pb}^{2+}} = 2\text{pH} + 6.12. \tag{18}$$

Figure 7 is the pM-pH of  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  system obtained from Eqs. 13-18, where  $\text{Al}^{3+}$  exists on the left of blue line and  $\text{Al}(\text{OH})_3$  is on the other side. The  $\text{RE}^{3+}$  and  $\text{RE}(\text{OH})_3$  are on the left and right of black line, respectively. The precipitating pH of  $\text{Al}(\text{OH})_3$  is lower than that of  $\text{RE}(\text{OH})_3$ , suggesting that most of  $\text{Al}(\text{OH})_3$  can be precipitated while little RE precipitate is formed, especially at pH 5 (Chi and Tian,



2008). Therefore,  $\text{Al}^{3+}$  can be removed by the  $\text{NH}_4\text{HCO}_3$ . However, it is not fit for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  due to the higher precipitating pH of  $\text{Cu}(\text{OH})_2$  and  $\text{Pb}(\text{OH})_2$  than  $\text{RE}(\text{OH})_3$ . Since RE ions do not react with  $\text{S}^{2-}$  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 ( $\text{PbS}$ ) and red ( $\text{CuS}$ ) lines are upper than the black line ( $\text{RE}(\text{OH})_3$ ), indicating an efficient removing way of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by sulfide precipitation method.

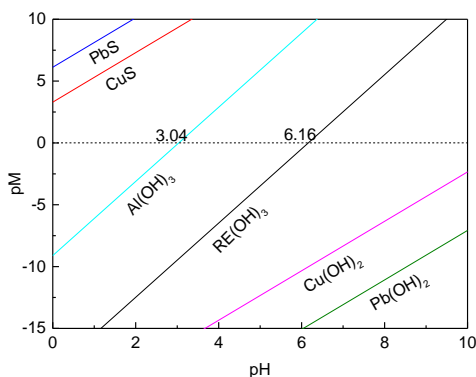


Fig. 7. pM-pH diagram of  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  in  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  system

### One-step purification of impurities from the rare earth leachate by the compound of $\text{NH}_4\text{HCO}_3$ and $\text{Na}_2\text{S}$

According to the discussion of impurity ions behavior and the above experiment results, it is found that  $\text{NH}_4\text{HCO}_3$  is beneficial to  $\text{Al}^{3+}$  removal, but imperfect to remove  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  than  $\text{Na}_2\text{S}$ . Furthermore,  $\text{NH}_4\text{HCO}_3$  has a less bad influence than  $\text{Na}_2\text{S}$  on the following RE industrial production, and is more environmentally friendly. The compound of  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  is thus proposed to remove impurity ions from the RE leachate. Different compounds of  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  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  $\text{Na}_2\text{S}$  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  $\text{Al}^{3+}$  and the RE recovery are very low, although the removal rates of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  are very high, indicating an imperfect purification effect of the  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  compound at volume ratio of 5:5 and 6:4. From Figure 8(c), the removal rate of  $\text{Al}^{3+}$  is lower than 60% among the tested pH range, although it increases with the increasing of  $\text{NH}_4\text{HCO}_3$  consumption compared to Fig. 8(b), suggesting the compound of  $\text{NH}_4\text{HCO}_3:\text{Na}_2\text{S} = 7:3$  is also unsuitable to remove impurity ions. For the

$\text{NH}_4\text{HCO}_3:\text{Na}_2\text{S} = 8:2$  in Fig. 8(d), the removal rates of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Al}^{3+}$  increase with the increasing pH. At pH about 6.0, the removal rate of  $\text{Al}^{3+}$  is up to 70%, the  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  are higher than 86%, but the RE recovery is lower than 65%. A lot of rare earth resources are lost indicating that the  $\text{NH}_4\text{HCO}_3:\text{Na}_2\text{S} = 8:2$  is also unsuitable to remove impurity ions from the RE leachate.

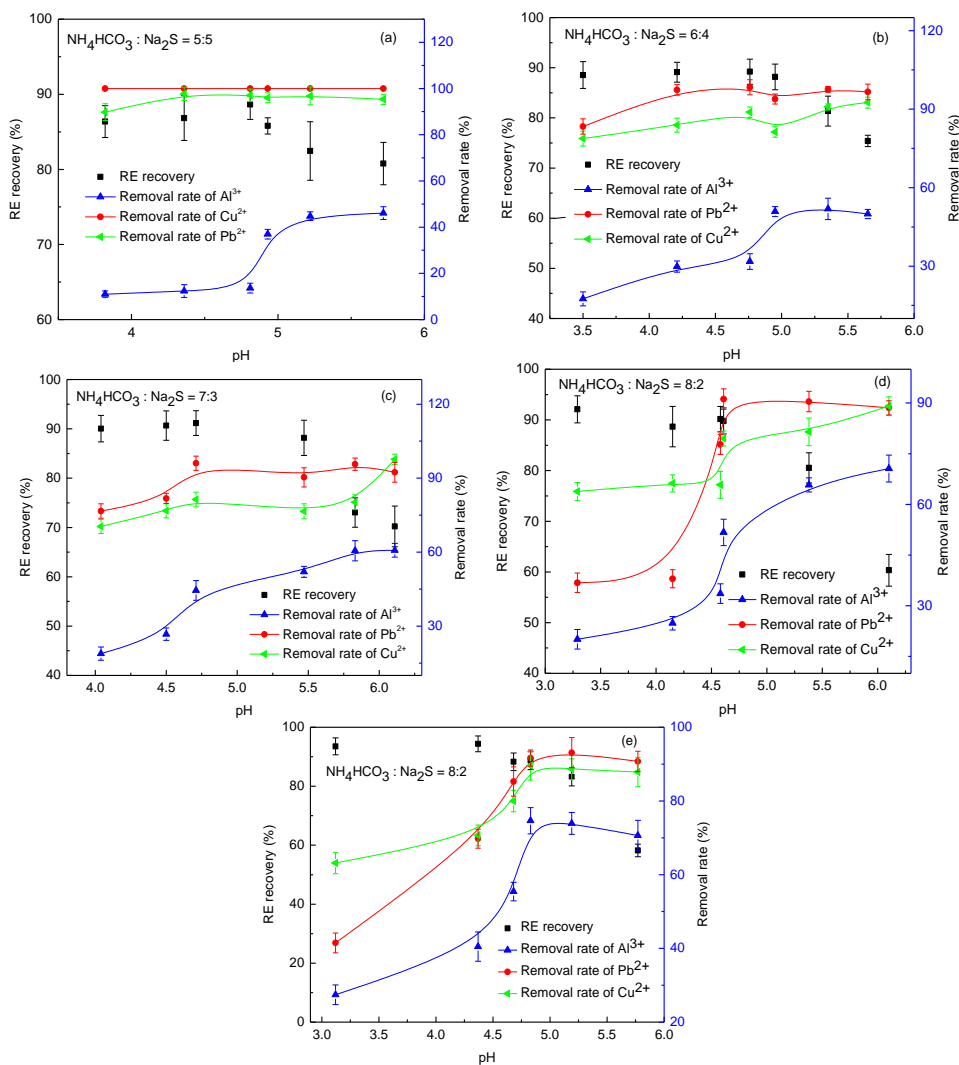


Fig. 8. RE recovery and removal rates of  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  as a function of pH (compound/leachate volume ratio of 0.05:1; compound concentration 0.1 M; precipitation time 30 min; room temperature); (a)  $\text{NH}_4\text{HCO}_3:\text{Na}_2\text{S}$  volume ratio of 5:5; (b)  $\text{NH}_4\text{HCO}_3:\text{Na}_2\text{S}$  volume ratio of 6:4; (c)  $\text{NH}_4\text{HCO}_3:\text{Na}_2\text{S}$  volume ratio of 7:3; (d)  $\text{NH}_4\text{HCO}_3:\text{Na}_2\text{S}$  volume ratio of 8:2; (e)  $\text{NH}_4\text{HCO}_3:\text{Na}_2\text{S}$  volume ratio of 9:1

Figure 8(e) shows that the removal rates of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Al}^{3+}$  increase with the increasing pH at the volume ratio of  $\text{NH}_4\text{HCO}_3:\text{Na}_2\text{S} = 9:1$ . The RE recovery decreases with the pH increase. At the pH around 4.8-5.1, the removal rates of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Al}^{3+}$  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  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Al}^{3+}$  are removed. Furthermore, the pH of the compound of  $\text{NH}_4\text{HCO}_3$  and  $\text{Na}_2\text{S}$  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  $\text{NH}_4\text{HCO}_3$  as precipitator was not effective enough to remove impurity ions especially  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  from RE leachate, and  $\text{Na}_2\text{S}$  as the precipitator was beneficial to the precipitation of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , but fail to precipitate  $\text{Al}^{3+}$ . For a better impurity purification, the compound of  $\text{NH}_4\text{HCO}_3:\text{Na}_2\text{S}$  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,  $\text{NH}_4\text{HCO}_3:\text{Na}_2\text{S}$  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  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Al}^{3+}$  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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