

## Study on non-saponification extraction process for rare earth separation

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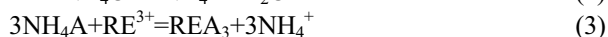
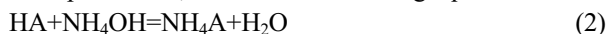
**Abstract:** The purpose of this study was to overcome the disadvantages of ammonia-nitrogen wastewater pollution and high cost of sodium saponification in rare earth separation process. The study focused on the non-saponification extraction technology with magnesia. The influences of the content and particle size of magnesia, reaction time, reaction temperature, and O/A on cerium extraction rate were also discussed. The results showed that the hydrogen ions of extractant were exchanged by rare earth ions when organic extractant and rare earth solution were mixed with magnesia powder, and then the exchanged hydrogen dissolved magnesia to make the acidity of the system stable. The magnesium ions were not participated in the extraction reaction. Non-saponification extraction process of rare earth had been realized. The cerium extraction rate could reach up to 99% in single stage within the optimal reaction conditions.

**Keywords:** magnesia; non-saponification; solvent extraction; rare earths

As their unique physicochemical properties, rare earth elements are considered indispensable in modern industry. They are extensively used in many areas such as new energy, new materials, energy conservation and environmental protection, aeronautics, astronautics and electronic information. The solvent extraction with acidic extractants, including P<sub>204</sub>, P<sub>507</sub>, is generally used for separation and purification of single rare earth in industry<sup>[1-3]</sup>. The acidic extraction capacity of the extractant is inversely proportional to equilibrium acidity of aqueous phase.



So, the extractant should be saponified in advance to remove hydrogen ions using such inorganic alkali as ammonia or sodium hydroxide to increase RE load amount in organic extractant and ensure capacity in large scale production, described as following equations:



HA denotes organic extractant. RE<sup>3+</sup> denotes trivalent rare earth ion.

It can be seen that the exploitation of rare earth has brought about significant environment problems, especially ammonia-nitrogen wastewater pollution because of saponification with ammonia<sup>[4,5]</sup>. In China, RE separation capacity is more than 15 million tons (REO) per year. Since ammonia is usually used for organic extractant as

saponifier, over 100 thousand tons of liquid ammonia should be consumed per year. Currently, a part of rare earth separating enterprises take caustic soda solution instead of ammonia as saponifier or introduce the end-treatment, but a part of them still use ammonia saponification and don't recycle at all, which leads to serious pollution problems<sup>[6,7]</sup>.

For the past ten years, General Research Institute for nonferrous metals (National Engineering Research Center for Rare Earth Materials) have innovatively developed a pretreatment method of the blank acidic extractant to resolve the pollution problems in the rare earth separation process because of saponification with ammonia<sup>[8,9]</sup>. In the pretreatment method, the organic extractant is directly mixed with RE solution and alkaline earth metal compound powder containing Mg and/or Ca, or with slurry (produced with water), for pre-extraction. Based on previously work, mechanism in the pretreatment process was studied that P<sub>507</sub> and CeCl<sub>3</sub> solution were mixed with powder of magnesia. In addition, suitable reaction conditions were also discussed in this paper.

## 1 Experimental

### 1.1 Reagents

CeCl<sub>3</sub> solution was prepared by dissolving Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>

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(99.95%, Guosheng Rare Earth Co., Ltd., Jiangsu) in HCl solution. 2-ethylhexyl phosphoric acid, mono (2-ethylhexyl) ester ( $P_{507}>95\%$ , Luoyang Aoda Co., Ltd.) was used as an extractant and was diluted with sulfonated kerosene. All chemicals, for example magnesia (AR, Sinopharm Chemical Reagent Co., Ltd.) used in the study, were of analytic reagent grade.

## 1.2 Experiment methods

$CeCl_3$  solution and organic solutions, also with a certain content of powder of magnesia, were placed in a separatory funnel and shaken at a certain temperature by vibration equipment. They were rapidly hierarchical by centrifuge (Eppendorf Centrifuge 5804(R)/5810(R)) in a certain period of time. Magnesium and rare earth concentration in organic were stripped by HCl and the strip liquor was tested using inductively coupled plasma spectrometer (SHIMADZU ICPS-7510). Magnesium ion extraction rate was defined as

$$E_{Mg} = \frac{C_{Mg(O)}}{C_{Mg(A)}}$$

$E_{Mg}$  denotes magnesium ion extraction rate.  $C_{Mg(O)}$  denotes the concentration of magnesium loaded in organic.  $C_{Mg(A)}$  denotes the initial concentration of magnesium chloride while  $C_{Mg(A)}$  denotes the initial concentration of MgO in experiment No. 3 and No. 5 in mechanism studies.

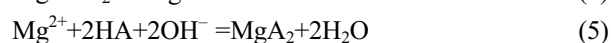
## 2 Results and discussion

### 2.1 Mechanism studies

There are two following possible reaction mechanisms in the pretreatment process that organic extractant and rare earth solution are mixed with powder of magnesium oxide.

#### 2.1.1 Reaction mechanism 1

Magnesium oxide obtains hydroxide ions and magnesium ions by hydrolysis (Eq. (4)). Magnesium ions are extracted into organic phase, and then neutralization reaction happens between the exchanged hydrogen ion and hydroxide (Eq. (5)), so that the acidity of the aqueous phase remains stable. Magnesium ions loaded in organic phase are exchanged by rare earth ions in the aqueous phase (Eq. (6)). This is the saponification reaction mechanism that acidic extractant reacts with alkaline matter obtaining water and organic salt.



HA denotes organic extractant.  $RE^{3+}$  denotes trivalent rare earth ion.

Eq. (5) is a kind of typical saponification reaction, which is the same as Eq. (2). The extractant is saponified in advance to remove hydrogen ions, forming or-

ganic salt  $MgA_2$ , and then magnesium ions loaded in organic phase were exchanged by rare earth ions. This is a saponification extraction process.

#### 2.1.2 Reaction mechanism 2

The second reaction mechanism, the hydrogen ions of extractant is exchanged by rare earth ions (Eq. (7)), rare earth ions are extracted into organic phase, then the exchanged hydrogen ions dissolve magnesium oxide, producing water and magnesium ions (Eq. (8)).



HA denotes organic extractant.  $RE^{3+}$  denotes trivalent rare earth ion.

Because of its existence of Eq. (8), the acidity of the aqueous phase could be stable, so Eq. (7) could be towards right. The saponification Eq. (5) is avoided and there are not forming organic salt, namely  $MgA_2$ . According to the reaction mechanism 2,  $REA_3$  was directly formed, so it is a non-saponification extraction process.

A series of experiments were carried out in the range of No. 1–No. 6, to study the mechanism of the pretreatment process. No. 1 and No. 2 in Fig. 1 show the extraction reaction results of magnesium ions and cerium ions with  $P_{507}$  respectively. The extraction rate of cerium ions was 18.10%, and higher than the magnesium ion ~2.14% when the system attained balance within a short period of time. It is clear that the extraction capacity of cerium ions is much larger than magnesium ions, which is consistent with the regularity of the extraction ability of the metal ions by  $P_{507}$ <sup>[10–14]</sup>.  $P_{507}$  extraction ability of the trivalent metal ion is greater than the divalent metal ion under the same conditions<sup>[15,16]</sup>. No. 4 and No. 1 in Fig. 1(a) and No. 5 and No. 2 in Fig. 1(b) show that the addition of MgO could improve the extraction rate of rare earth ions and magnesium ions because of the stability of the acidity in the aqueous phase.

Comparison on the data of No. 5 and No. 6 in Fig. 1 concluded that the adding of  $MgCl_2$  had nothing to do with the extraction rate of cerium ions. Because of the difference of the extraction ability between magnesium ions and cerium ions, large amount of cerium ions and a little of magnesium ions were extracted into the organic phase firstly in the beginning of the reaction in the existence of cerium ions and magnesium ions, and then magnesium oxide tended to be dissolved in the exchanged hydrogen ion by cerium ions, so it is a process that most of the  $CeA_3$  was formed directly rather than replace the magnesium loaded in organic. However, magnesium ions loaded in organic in the beginning of the process, replaced partly by cerium ions, had reduced from 3% to about 1% according to Mg extractant efficiency as calculated and the extraction rate of cerium ions increased greatly from 25% to above 70% with the increase of the reaction time, the extraction rate of cerium ions is as much as over 70 times than the extraction

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