



Complete separation of aluminium from rare earths using two-stage solvent extraction



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ARTICLE INFO

Keywords:

Aluminum
Rare earth
Separation
Naphthenic acid
Octyl phenoxy iso propionic acid

ABSTRACT

To remove aluminum (Al) from rare earth element (REE) especially light rare earth element (LREE), octyl-phenoxy isopropionic acid (OPIPA) has been developed for the liquid-liquid extraction separation of Al from REE in this study. Using specific extraction experiment and infrared spectra analysis, the stoichiometry of saponified octyl-phenoxy isopropionic acid (S-OPIPA) to Al is indicated to be 3:1. The results of extraction investigation show that the separation effects of Al and REE arrive best when the initial water solution is pH = 3. The stripping experiment shows that sodium hydroxide is the best stripping agent. The extraction abilities of Al by OPIPA, naphthenic acid (NA), saponified OPIPA (S-OPIPA) and saponified naphthenic acid (S-NA) are compared at the pH values of 1, 2, 3, which indicates the importance of saponification. The loading capacities of S-NA and S-OPIPA reach the maximum values of 1.82 g/L and 1.85 g/L, respectively. It is found that S-NA is easy to be emulsified, while S-OPIPA reveals excellent phase separation behavior for the Al solution with the high concentration. The difference indicates that S-OPIPA is more suitable for the massive removal of Al. In the separation process of simulated REE ore leaching solution, the Al concentration can be lowered to zero after two stages of Al removal with S-OPIPA and S-NA sequentially, and REE recovery rate of 86.43% with a purity of 99.69% is achieved.

1. Introduction

Rare earth elements (REEs) are essential for hundreds of applications in the fields of permanent magnets, fluorescent materials, batteries, laser crystals, alloys, catalysts, superconductors, etc. The versatility and specificity have provided REEs with considerably technological, environmental, and economic importance. The value of REE products is often affected by the purity of products, so the separation of impurities from REEs is very important in the production process.

However, in many rare earth mineral leaching solutions, Al and Fe are often abandoned impurity, and the separation of Al from rare earth especially light rare earth is difficult. Before carrying out the separation research of Al and rare earth, as shown in the following table, some Al separation researches were consulted to analyze the separation effect of Al (Table 1).

Some minerals contain Al and REEs together, such as the weathered crust elution-deposited REE ore (Tian et al., 2010). In the treatment

processes of these minerals, the extraction and recovery of REEs should be focused on. Unfortunately, Al is often difficult to remove from the leaching solution as an abandoned impurity. This is actually not conducive to the recovery of REEs. For a long time, the weathered crust elution-deposited REE ore in southern China is used for the extraction of REEs, but the separation of Al and REEs has been perplexing industrial production.

In fact, there are reports on separation or comprehensive recycling of Al and REEs in the literatures. In the process of FCC catalyst waste slag treatment, by stepwise leaching and oxalic acid precipitation, the recoveries of REEs and Al were 37.9% and 90.0%, respectively (Qiu and Wei, 1992). On the FCC catalyst waste slag, another report shows that REEs and Al in the leachate were recovered in the forms of amorphous hydroxides by a stepwise neutralization precipitation, and the recovery ratios reached 91.3% and 90.2%, respectively (Wang et al., 2017a). A method for recycling REE and Al from ion-absorption rare-earth ore to obtain ore leaching solution was also reported (Xiao et al., 2017).

The leaching solution from weathered crust elution-deposited REE

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<https://doi.org/10.1016/j.hydromet.2018.06.004>

Received 5 January 2018; Received in revised form 31 May 2018; Accepted 14 June 2018

Available online 15 June 2018

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Table 1
The studies on Al separation.

Resources	Valuable components	Separation method and effect	Ref.
Kaolin	Al ₂ O ₃ , SiO ₂	K ₂ SiF ₆ and Na ₃ AlF ₆ were recovered by precipitation with alkaline salts from the leach liquor.	(Pinna et al., 2017)
Coal gangue	Al ₂ O ₃ , SiO ₂	The separation of AlCl ₃ ·6H ₂ O from acid leaching solution by crystallization was an effective method. It reached > 85% of the maximum crystallization at the volume ratio of concentrated HCl to the solution exceeding 2.25.	(Pan and Ma, 2010) (Guo et al., 2015)
Spent catalysts containing platinum group metals	Fe, Al and Pt	Two extraction chromatographic steps extracted most of Fe and 90% of Al with PC88A resin from the solution, while Pt was not extracted.	(Sun et al., 2010)
Red mud	Al ₂ O ₃ , Na ₂ O, SiO ₂ , Fe ₂ O ₃	A mild hydro-chemical process to extract Al ₂ O ₃ in red mud to produce sodium aluminate hydrate was investigated. As for red mud slurry or filter cake from the Bayer process, 95% of Na ₂ O and 70% of Al ₂ O ₃ could be recovered from the red mud.	(Zhong et al., 2009) (Cresswell and Milne, 1984; Cresswell and Milne, 1982)
Fly ash	Al ₂ O ₃ , SiO ₂ , Fe ₂ O ₃ , CaO	A sulfuric acid leaching process to extract metallurgical level alumina from fly ash through a high-pressure sulfuric acid leaching, removing iron, crystallizing and roasting processes was studied. A mixture of HAFA and Na ₂ CO ₃ was sintered at temperature of 800–900 °C, and the alumina extraction was up to 96.73%. The effects of leaching conditions on the alumina were studied, by optimizing the leaching conditions, the alumina extraction ratio reached 91.3%.	(Lv et al., 2013) (Ding et al., 2006; Zhang et al., 2005) (Li et al., 2014)

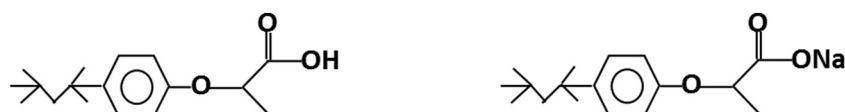


Fig. 1. The structures of studied extractants.

octyl-phenoxy isopropionic acid

saponified octyl-phenoxy isopropionic acid

ore often contains Al, which is difficult to be separated from the target REEs. To resolve the problem, an effective extractant of naphthenic acid, was studied for the solvent extraction of Al. At the pH value of 3.0 and the initial Al concentration of 0.15 mol/L, naphthenic acid revealed a highest extraction rate of Al in the absence of emulsification (Yang and Qiu, 2017). However, there is still few method reported for the solvent extraction of Al, and the extractant for Al is also lacking. Therefore, it is worthwhile to develop more extractants for the efficient extraction of Al. As shown in Fig. 1, a new type of phenoxy carboxylic acid extractant has been prepared in this lab. The developed extractant after saponification reveals stronger extraction ability to Al. Thus, a series of studies on the extraction and separation of Al and REEs are reported in this article.

2. Experimental

2.1. Reagents and apparatus

Naphthenic acid was obtained from Luoyang Aoda Chemical Co., Ltd. (China), which was purified as described elsewhere (Xue and Li, 1992). Heptane was employed as the diluent during the extraction experiments. The filtered leaching solution used in the REE component detection was obtained by injecting 25 mL nitrohydrochloric acid into 1 g weathered crust elution-deposited REE ore, then the mixture was digested by microwave digestion apparatus for 3 h. Inductively coupled plasma optical emission spectroscopy (ICP-OES, Horiba Ultima 2) was used to determine the concentrations of metal ions in aqueous phase. The concentrations of acidic extractants were titrated by standard solution of sodium hydroxide (Wang et al., 2011). The concentration of free H⁺ was determined by volumetric titration with standard NaOH solution. NaOH solutions with various concentrations were used as the saponification agents.

2.2. Synthesis of OPIPA

Octylphenol (20.7 g, 0.1 mol), NaOH (4.0 g, 0.1 mol), and 50 mL of absolute ethanol were added to a 250 mL round-bottomed flask equipped with a condenser and magnetic stirring bar, and followed by stirring at 60 °C with the protection of argon for 30 min (avoid oxidation of octylphenol) to get phenol sodium solution. Slowly, under stirring, drop by drop a solution of sodium 2-chloropropionate (13.5 g, 0.1 mol dissolved in 15 mL distilled water) was added to the center of previous phenol sodium solution for > 30 min at 100 °C and the reactant was stirred for another 1 h until there was no raw material left. It should be noted that the pH value of whole process was kept from 10 to 12. A large amount of solid was produced in the reaction. The resultant solid-liquid mixture was sequentially acidified with 6 mol/L HCl after cooled to room temperature and then separated by a separating funnel to remove the aqueous phase. In the process of separation, a proper amount of ether could be added to accelerate the separation of organic phase and aqueous phase. Then the organic phase was washed several times until the aqueous phase pH was about 3. The product was obtained by evaporating the organic phase with a rotary evaporation apparatus and then drying by vacuum drying oven to give the final buff solid (86.8% yield).

OPIPA used in this study was characterized by NMR. ¹H NMR (500 MHz, DMSO) δ 12.93 (s, 1H), 7.28 (m, 2H), 6.76 (d, *J* = 10.0 Hz, 2H), 4.75 (s, 1H), 1.68 (s, 2H), 1.49 (s, 3H), 1.30 (s, 6H), 0.70 (s, 9H); ¹³C NMR (126 MHz, DMSO) δ 173.73 (s, 1C), 155.50 (s, 1C), 142.36 (s, 1C), 127.36 (s, 2C), 114.36 (s, 2C), 71.86 (s, 1C), 56.77 (s, 1C), 38.07 (s, 1C), 32.47 (d, *J* = 5.3 Hz, 1C), 32.04 (s, 3C), 31.88 (s, 2C), 18.79 (s, 1C). In this study, the concentration of OPIPA was determined by the means of titration with sodium hydroxide. The pKa value of OPIPA (pKa = 5.19) was determined by pH titration method in 75 (v/v) % alcohol solution with 0.0505 mol/L NaOH at 25 °C.

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