



Kinetics of column leaching of rare earth and aluminum from weathered crust elution-deposited rare earth ore with ammonium salt solutions



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ABSTRACT

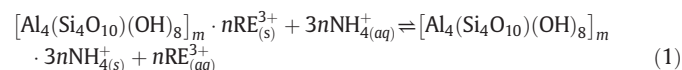
In this study, a mixture of ammonium chloride and ammonium nitrate was used as a leaching agent to improve the leaching efficiency and leaching rate of rare earth (RE) from weathered crust elution-deposited RE ore. By performing the column leaching experiments, effects on the leaching efficiency and leaching rate of RE, such as the molar ratio of the two components, concentration of ammonium (NH_4^+), liquid/solid ratio and pH of the leaching agent, were investigated. In addition, the effects of above parameters on the leaching performance of aluminum (Al), which is the main impurity in RE leachate, were also studied. It was found that the optimal conditions of column leaching were a 1:1 (molar ratio) of NH_4Cl and NH_4NO_3 , 0.2 mol/L of ammonium concentrate, 2:1 liquid:solid (mL/g) and a leaching agent with a pH between 4.0 and 8.0. The maximum leaching efficiency of RE could be 91%. Moreover, the leaching equilibrium time for RE was 25 min shorter than for Al, which is of benefit to reduce the leaching of Al. The leaching process was analyzed using the shrinking-core model to examine the kinetic parameters and rate controlling step. The leaching rate was controlled by the inter-diffusion of the reactants and leaching products through the mineral porous layer. An empirical equation based on the apparent rate constant and ammonium concentration was established for process optimization, and the reaction orders were 1.92 for RE and 1.48 for Al. The results of this study may play a vital role in developing a high efficient leaching technology for weathered crust elution-deposited RE ore.

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1. Introduction

Weathered crust elution-deposited rare earth (RE) ore, also known as ion adsorbed RE ore, is a unique mineral resource with significant commercial value in China. It is widely distributed in southern China, in provinces such as Jiangxi, Guangdong, Fujian, Hunan, Yunnan, Guangxi and Zhejiang. Wide attention was given to explore this ore because it is rich in middle and heavy rare earth elements (REE) (Chi et al., 2012). In a warm humid climate, the rocks originally containing the RE minerals are weathered and converted to clay minerals by biological, chemical and physical effects. During the same progressive geological weathering leaching process, RE minerals are dissociated to be hydrated or hydroxyl hydrated RE ions and further adsorbed by the clay minerals during the natural migration of water (Nesbitt, 1979; Wan and Liu, 2005). It is noted that 70% to 95% of RE exist in the ion phase and are adsorbed by the clay minerals and can be exchanged from the weathered crust elution-deposited RE ore with an electrolyte solution using the ion-exchange method (Chi et al., 2005; Kul et al., 2008). The main clay minerals are aluminosilicate, which can be

described as $[\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8]_m$. The leaching chemical reaction with an ammonium salt is written as (Tian et al., 2010b):



where s and aq represent the solid phase and aqueous phase, respectively.

This leaching mechanism of the RE has been further proven by Moldoveanu and Papangelakis (2012). Moldoveanu and Papangelakis (2013) found that the extraction kinetics are very fast and can be completed in 5 min in the stir condition. The leaching process is a typical noncatalytic heterogeneous reaction in liquid–solid systems.

The initial leaching agent employed in the leaching process of the weathered crust elution-deposited RE ore was sodium chloride (Chi and Tian, 2008). It was found that the leachate using sodium chloride contained a large amount of impurities, such as Al, Mg, K, and Ca that obviously increased the cost to remove the impurities and decreased the purity of the RE product. Moreover, the residual sodium chloride in the RE orebody caused soil salinification. With the development of additional leaching agents, ammonium sulfates displaced sodium chloride and is widely employed because of its high leaching efficiency and

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good quality RE product (Chi and Wang, 2014; Liu et al., 2013; Georgiana et al., 2012). The drawback of using ammonium sulfate is that it has a slow leaching rate for RE attributed to its poor permeability in RE orebody. Therefore, it is important to look for other leaching agents with high permeability.

Previous researchers have reported novel leaching agents for weathered crust elution-deposited RE ore (Li et al., 2009; Yao et al., 2005; Zhang et al., 2013, 2014) that mainly focused on improving the leaching efficiency. Limited work has been performed on the leaching kinetics of RE and the control of leachate impurities. Aluminum ions, which always leach out with RE, account for 35% to 75% of the total amount of impurities in the leachate. These Al ions decrease the quality of the RE product, increase the consumption of precipitant and sometimes even retard the crystallization of the RE carbonate (Chi and Xu, 1999; Chi et al., 2003).

Previous studies revealed that the exchangeability and permeability of three ammonium salts occur in the following order: $(\text{NH}_4)_2\text{SO}_4 < \text{NH}_4\text{Cl} < \text{NH}_4\text{NO}_3$ (Chi and Wang, 1990). Ammonium nitrate seems to have the highest potential as the leaching agent because it has the highest exchangeability and permeability. Actual application of pure NH_4NO_3 is greatly limited, however, because of its high cost. To lower the cost of the leaching agent, this study examined the effect of a mixture of NH_4Cl and NH_4NO_3 , molar ratio, concentration of ammonium (NH_4^+), liquid/solid ratio and pH of the leaching agent on the leaching efficiency and leaching rate of RE. Leaching performance of aluminum (Al), which is the primary impurity ion in the leachate, was also investigated. In addition, an empirical equation based on the apparent rate constant and ammonium concentration was established, which may lead to further optimization of the leaching process.

2. Materials and methods

2.1. Materials

The RE ore samples were collected from Dingnan (DN) in the Jiangxi Province, China. Gangue minerals in the weathered crust elution-deposited RE ore are mainly quartz, potash feldspar, plagioclase, kaolinite and white mica (Chi and Tian, 2008). The RE ore sample was air dried at 70 °C for 8 h. The dried sample was shaped into a cone. Then, it was flattened by a trowel and quartered. Finally, the last two diagonal quarters were collected and remixed. The sample preparation steps were repeated until the fully mixed sample was large enough for the experiments.

All chemicals in this study were analytical grade chemicals purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The deionized water was produced by a water purification system.

2.2. Column leaching experiments

In each column leaching experiment, 250 g of the RE ore sample was packed uniformly in a glass leaching column with an inner diameter of 45 mm and a column length of 500 mm. A sand core filter plate was fixed to the bottom of the leaching column to retain the soil particles and two layers of filter papers were placed on the top of the RE ore sample to resist preferential flow. The leaching agent was added from the top of the column at a constant flow rate by a peristaltic pump. Leachate was collected from the bottom of the column and the concentrations of RE and Al were analyzed using the ethylenediaminetetraacetic acid (EDTA) titration method.

2.3. Analytical methods

The total content of RE in the leachate was determined using EDTA titration by using xylenol orange as the indicator and hexamethylene tetramine as the buffer. After that, excess EDTA solution was added into the studied solution sample and placed in a water bath at 90 °C

for 10 min. Then, the Al content was analyzed using titration with a known concentration of zinc solution (Li et al., 2009). The error of the titration method was within $\pm 2\%$. The leaching efficiency (α) was calculated using the following equation:

$$\alpha = \frac{CVM_{\text{AO}_{3/2}}}{mw} \times 100\% \quad (2)$$

where C (mol/L) is the concentration of ions (A^{v+}) in the leachate; V (L) is the volume of the leachate; M (g/mol) is the relative molar mass of $\text{AO}_{3/2}$; A represents RE or Al; m (g) is the mass of the ore sample; and w (%) is the mass fraction of the exchangeable A_2O_3 in the ore sample.

3. Results and discussion

3.1. Characterization of the RE ore

The particle size distribution of the experimental sample was shown in Table 1. Chemical composition of the RE ore was analyzed using X-ray fluorescence (Axios Advanced, Panalytical B.V.) shown in Table 2. The results reveal that the RE ore contains 0.10% RE and 19.53% Al. It was reported that the RE can exist either in aqueous soluble, ion-exchangeable, colloid sediment or mineral state. However, only the exchangeable state can be exchanged from the RE ore into the solution by a cation with a pH of 4 to 8 (Chi et al., 2005). States of Al include soluble, exchangeable, adsorption inorganic hydroxyl, iron oxide combined, interlaminar, non-crystalline metasilicate and mineral state. To estimate the maximum exchangeable capacity of the RE ore, a column leaching experiment was performed with 250 g of RE ore sample with 0.4 mol/L $(\text{NH}_4)_2\text{SO}_4$ solution at pH 5.5 to 6 (Chi and Tian, 2008). Sampling during the leaching test continued until the concentration of the RE and Al in the leachate was below the detection limit. Chemical composition of the leachate was analyzed using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700 ×, Agilent Technologies Inc.). The exchangeable components test was duplicated and the error was found to be within $\pm 2\%$. The results of this leaching test are listed in Table 3.

As shown in Table 3, the maximum exchangeable RE grade is 0.09%, which accounts for 90% of the total RE. This demonstrates that 90% of the RE in this ore exists in the ion-exchangeable state. The partitioning of the exchangeable RE in the leachate was analyzed by ICP-MS as well; the results were shown in Table 4. This reveals that 52% of the RE is middle and heavy RE ions.

The exchangeable Al takes only 0.077% of the total amount. However, this small amount of leached-out Al still has a negative effect on the downstream production; thus, the leaching process of Al should be studied and optimized.

3.2. Leaching kinetics with different leaching agents

To examine the feasibility of a mixture of NH_4Cl and NH_4NO_3 as a leaching agent, three single ammonium salts ($(\text{NH}_4)_2\text{SO}_4$, NH_4Cl and NH_4NO_3) and mixed ammonium salts (NH_4Cl plus NH_4NO_3 with a molar ratio of 1:1) were used to treat the RE ore under the condition of 0.2 mol/L of ammonium concentration, 2:1 for liquid/solid (mL/g) and pH 5.5–6.0 of the leaching agent.

Fig. 1(a) shows that the maximum leaching efficiency for RE occurs in the following order: $(\text{NH}_4)_2\text{SO}_4$ (82.91%) < NH_4Cl (86.27%) < NH_4NO_3 (89.66%) < $\text{NH}_4\text{Cl}/\text{NH}_4\text{NO}_3$ (90.96%). Among the three single ammonium salts, NH_4NO_3 has the highest leaching efficiency, while $(\text{NH}_4)_2\text{SO}_4$ has the lowest efficiency. These results may be explained by the fact that the exchangeable capability of NH_4^+ in the leaching agents is relevant to their complexing ability. Chi and Wang (1990) reported that the complexing ability of the three anions with RE was in the following order: $\text{SO}_4^{2-} < \text{Cl}^- < \text{NO}_3^-$. The

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