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Compound leaching behavior and regularity of ionic rare earth ore

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ABSTRACT

Ammonium sulfate in situ leaching process is the most widely used extraction technology for ionic rare earth (RE) ores. Although the leaching process is simple, the leaching rate is satisfactory; moreover, the leaching solution has high impurities, serious ammonia pollution, and other problems. The leaching rate and leaching efficiency using a single ammonia-free leaching agent are low, particularly for low-grade complex ores. In this study, a leaching experiment and kinetic analysis of a combined leaching agent for an ionic RE ore with low grade and high impurity content were carried out.

The results show that the leaching rate of RE^{3+} is 97.58%, and the concentration of Al^{3+} in the leaching solution is 0.016 g/L when a combined leaching agent composed of QZX-02 and ammonium sulfate (mass ratio of 7:3) was used to leach the ionic RE ore. Compared with using ammonium sulfate alone, the leaching rate of RE increased by 8.96%, and the concentration of Al^{3+} decreased by 0.069 g/L. Both of the leaching process of ammonium sulfate and the combined leaching agent are controlled by internal diffusion kinetics, and the apparent activation energies are 8.59 kJ/mol and 7.34 kJ/mol, respectively. The lower apparent activation energy makes the combined leaching agent possess a higher leaching efficiency. The analysis of Fourier transform infrared (FTIR) spectras and scanning electron microscopy (SEM) images indicate that the combined leaching agent and impurity ions could produce carboxylic acid organic compounds on the surface of clay minerals, with the result that the leaching of impurity ions is suppressed and the leaching efficiency of RE ions is improved. The application of this combined leaching agent can alleviate the ammonia pollution caused by the ammonium sulfate leaching process and effectively improve the utilization rate of RE resources.

1. Introduction

Ionic rare earth (RE) ores, which are also known as ion-adsorption RE ores or weathered crust elution-deposited RE ores, are resources of strategic importance. They are mainly distributed across China's Jiangxi, Fujian, Guangdong, Guangxi, Hunan, and other southern provinces, of which the middle and heavy RE reserves accounted for 80% of the world's total RE reserves [1–3]. Although China is rich in RE resources, a large part has been destroyed, wasted, and lost [4,5] owing to the lack of mining technology in the early years and confusion in mineral resources management [6]. In addition, the widely used ammonium sulfate in situ leaching technology still has the problems of low leaching rate of RE ores, high content of impurity ions in the leaching solution, and pollution of ammonia–nitrogen. The challenge of improving the utilization rate of the existing RE mineral resources is an important subject for scholars in related fields.

In order to improve the extraction technology of ionic RE ores and increase the utilization rate of RE ore resources, a series of studies have been carried out by scientific researchers. Studies [7,8] showed that the leaching effect of ionic RE ores with two or more leaching agents is better than that by using a single leaching agent. Li et al. [9] studied the kinetics of leaching of an ionic RE ore with a mixture of ammonium salts. The results showed that the leaching effect of mixed ammonium salt, which was composed of ammonium sulfate and ammonium chloride with a mass ratio of 3:7, was the best. Zhang et al. [10] studied the leaching of an ionic RE ore with a complex ammonium salt; they found that a combined leaching agent composed of ammonium chloride, ammonium nitrate, and ammonium sulfate with a mass ratio of 4:5:6 has the best effect, and the higher the liquid–solid ratio and the slower the flow rate, the higher the leaching rate. In view of the ammonia–nitrogen pollution caused by the ammonium sulfate leaching technology, many scholars have carried out research on partial or complete replacement of ammonium sulfate as a leaching agent with ammonia-free leaching agents. Wang et al. [11] investigated the selection of a new ammonia-free leaching agent and the optimization of the column leaching technology for an ionic RE ore. The results showed that the average leaching rate of the RE ore was 98.40% when

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magnesium sulfate was used as a leaching agent. Several organic acids were used by Wu et al. [12] to leach an ionic RE ore; the results showed that compared with leaching the ionic RE ore with ammonium sulfate, the ratio of $(Gd/Yb)_N$ and $(La/Sm)_N$ decreased in the leaching solution, which shows that organic acids have a certain contribution to the element differentiation of ionic RE ores. Xiao et al. [13] used magnesium sulfate as a leaching agent to deal with an ion-adsorption type of RE ore to reduce or even eliminate ammonia–nitrogen emissions. The results showed that when the concentration of the leaching agent was 0.20 mol/L, the RE ore leaching efficiency could reach above 95% and the leaching efficiency of aluminum impurities could be reduced by 10% using magnesium sulfate compared with using ammonium sulfate. Some researchers try to strengthen the leaching technology of ionic RE ores by the action of magnetic, ultrasonic, and other external fields. Qiu et al. [14,15] showed that magnetic treatment of a leaching agent, water, and pulp by applying an external magnetic treatment device can change the physical and chemical properties of the water system, improve the leaching rate and efficiency of ionic RE ores, and reduce the consumption of leaching agent. Hu et al. [16] researched the effect of ultrasound on the leaching process of ionic RE ores. It was found that the cavitation of ultrasound can effectively enhance the leaching of RE ions and increase the leaching rate of RE ores. However, most of the above achievements have not been widely applied yet, at present. The existing extraction technology of RE ores still needs to be strengthened or improved by researchers.

The leaching kinetics of weathered crust elution-deposited RE ores has been studied by many researchers. Xiao et al. [17] investigated the use of magnesium sulfate instead of $(NH_4)_2SO_4$ as a leaching agent to alleviate ammonia–nitrogen pollution. It was found that the leaching kinetics of a weathered crust elution-deposited RE ore could be appropriately described by a pseudo-first-order model, and the apparent activation energy was calculated to be 8.90 kJ/mol. Tian et al. [18,19] showed that the leaching process of an ionic RE ore with ammonium sulfate solution could be described by a constricted nuclear model, and the leaching process was controlled by internal diffusion. He et al. [20] used a mixture of ammonium chloride and ammonium nitrate as a leaching agent to improve the leaching efficiency and leaching rate of RE from a weathered crust elution-deposited RE ore. They found that the maximum leaching efficiency of RE could reach 91%, and the leaching equilibrium time for RE was 25 min shorter than for Al, which is beneficial in reducing the leaching of Al. The leaching rate was controlled by the inter-diffusion of the reactants and leaching products through the mineral porous layer. Qiu et al. [21] studied the leaching kinetics of RE ions and Al^{3+} in an ammonia–nitrogen wastewater system with the aid of impurity inhibitors. The results showed that the leaching process of RE followed the internal diffusion kinetic model. When the temperature was 298 K and the concentration of NH^{4+} was 0.3 mol/L, the leaching reaction rate constant of the ionic RE was 1.72 and the apparent activation energy was 9.619 kJ/mol. The leaching rate was higher than that of a conventional leaching system with ammonium sulfate, which indicated that the ammonia–nitrogen wastewater system and the addition of impurity inhibitors could promote ionic RE leaching. The leaching kinetic process of Al^{3+} impurity did not follow either the internal diffusion kinetic model or chemical reaction control, but followed the hybrid control model, which was affected by a number of process factors. Although there are many reports on the leaching kinetics of ionic RE ores, the effect of apparent activation energy on the leaching efficiency of RE and the mechanism of enhancing the leaching efficiency of RE by a combined leaching agent are still not very clear.

In this study, a low-grade, high-impurity content of an ionic RE ore in Jiangxi Province was selected as the research object. A combined leaching agent with less ammonium was selected by a column leaching test. The leaching kinetics of the ionic RE ore using a combined leaching agent and ammonium sulfate was investigated, and the mechanism of enhancing the leaching efficiency of RE by the combined leaching agent was analyzed by Fourier infrared spectrum (FTIR) and scanning electron microscopy (SEM). The application of this combined leaching agent in ionic RE mine can ease ammonia pollution caused by the ammonium sulfate leaching technology and effectively improve the utilization rate of RE resources.

2. Experimental method

2.1. Materials and agents

The samples used were taken from an RE mine owned by Ganzhou Rare Earth Group Company. The ore samples appear as scattered irregular particles with diameters of 0.15 mm–0.25 mm and with gray color. Chemical analysis data of the multi-elements are listed in Table 1. These samples, with low grade of ion phase RE and high content of aluminum and iron impurity, are types of refractory ionic RE ores. The RE element (REE) distribution and REE occurrence of the samples are given in Tables 2 and 3.

As can be observed in Tables 2 and 3, the REE content of the RE ore is high, and 80.27% exists in the ionic state. According to the X-ray Diffraction (XRD) (DX-2700 type X-ray diffractometer, Dandong Fangyuan Instrument Co., China) results (Fig. 1), this ore contains many clay minerals, has poor crystallinity, and is mainly composed of quartz, albite, microcline, illite, montmorillonite, and halloysite. It is a typical ionic RE ore.

The ammonium sulfate, potassium chloride, ammonium chloride, QZX-02, and sulfuric acid used (with analytical grade) were all purchased from Sinopharm Chemical Agent Co., Ltd. QZX-02 is a type of organic acid double salt, which is a colorless to white orthorhombic crystal, non-toxic, soluble in water, and can form a complex with copper, iron, aluminum, lead, chromium, and other metal ions in an alkaline solution.

2.2. Leaching test of ionic RE ore

The column-leaching test of the ionic RE ore was conducted using the test equipment shown in Fig. 2. The test steps are as follows: first, a 500 g sample was added to the plexiglass column. Afterward, the leaching agent solution was supplied into the column at a constant

Table 1
Chemical multi-element analysis results/%.

RE_2O_3 (ionic)	Al_2O_3	Fe	K_2O	CaO	Na_2O	MgO	SiO_2	Other
0.071	19.05	1.31	5.87	0.032	4.19	0.047	41.95	27.48

Table 2
REE distribution/%.

REO	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7
Content	5.58	2.86	2.38	9.57	4.46	0.70	6.61	1.23
REO	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3	Total
Content	7.58	1.37	4.20	0.57	3.30	0.46	49.12	100

Table 3
REE occurrence/%.

Water-dissolving phase	Ionic phase	Colloidal sedimentary facies	Mineral phase	All
Trace	80.27	2.81	16.92	100.00