



Recovery of rare earths from weathered crust elution-deposited rare earth ore without ammonia-nitrogen pollution: I. leaching with magnesium sulfate



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ABSTRACT

The practice of in-situ leaching of weathered crust elution-deposited rare earth ore using $(\text{NH}_4)_2\text{SO}_4$ solution has revealed serious environmental problems such as ammonia-nitrogen pollution in water body and plant growth difficulties. The present study investigated the use of magnesium sulfate instead of $(\text{NH}_4)_2\text{SO}_4$ as the leaching agent in the recovery of rare earth elements to solve the problem of ammonia-nitrogen pollution. It was determined that the optimum leaching condition in 298 K, a flow rate of $0.60 \text{ mL} \cdot \text{min}^{-1}$, and $0.20 \text{ mol} \cdot \text{L}^{-1}$ magnesium sulfate solution, lead to 93% of total rare earth leaching efficiency and around 50% aluminum leaching efficiency. The results suggested that the magnesium sulfate was capable of producing identical recovery efficiency as $(\text{NH}_4)_2\text{SO}_4$ and reducing aluminum leaching efficiency at the same time. In addition, the leaching mechanism was analyzed with different kinetic models, it was determined that the leaching kinetics of the weathered crust elution-deposited rare earth ore could be appropriately described by Pseudo-first-order model, which indicated that the film diffusion was rate-limiting for the leaching process. The apparent activation energy was calculated to be $8.90 \text{ kJ} \cdot \text{mol}^{-1}$. However, the content of ion-exchangeable magnesium in rare earth washing tailings was 560 mg per kilogram soil. This would lead to an imbalance of ion-exchangeable calcium and ion-exchangeable magnesium, which would have a bad effect on the plant growth. Based on these findings, the synergic leaching with magnesium salt and calcium salt was identified as an excellent alternative leaching agent for further studies.

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1. Introduction

The ongoing development of advanced technologies resulted in an increasing demand for rare earth elements as they are extensively used in high strength permanent magnets, lasers, automotive catalytic converters, fiber optics/superconductors, and electronic devices, especially for the mid- and heavy rare earth (Wang and Li, 2003; Chen, 2011; Lahiri and Jha, 2009). The weathered crust elution-deposited rare earth ores are the main resources of mid-heavy rare earth in the world while they are mainly existing in China and most of them are located in Jiangxi, Fujian, Hunan, Guangdong, Yunnan and Guangxi provinces (Chi and Tian, 2008; Yasuo and Masaharu, 2006). The main form of rare earth elements (REEs) in the weathered crust elution-deposited rare earth ore is the ion-exchangeable phase adsorbed on clay minerals by electrostatic interaction, accounting for more than 80% of total rare earth (Chi et al., 2005). The conventional physical processing methods, such as flotation, magnetic, gravitational and electrostatic separation, are found to be ineffective in the recovery of rare earths from such sources, but the adsorbed rare earths can be exchanged with other

ions and desorbed when encountering with the more chemically active cations (Na^+ , NH_4^+ , H^+ , and Mg^{2+}) (Tian et al., 2010; Moldoveanu and Papangelakis, 2013).

For a long time, much effort has been engaged in the research and development of a series of hydrometallurgical processes for the specially weathered crust elution-deposited rare earth ores (Huang et al., 2005). There are three generations of leaching processes in the industry which have been developed along the green chemical leaching approach according to the ion-exchange property, including the first generation leaching process in pool with NaCl solution, the second generation leaching process in pool with $(\text{NH}_4)_2\text{SO}_4$ solution and the third generation in-situ leaching process with $(\text{NH}_4)_2\text{SO}_4$ solution. Moreover, new findings in laboratory investigation are recently focused on the intensification of leaching process by introducing the magnetochemistry, sesbania gum, compound leaching agent and on the impurities inhibited leaching (Qiu et al., 2008; Chi and Tian, 2008; Tian et al., 2013). However, the major leaching agent in these processes is still ammonium salt. The practice of in-situ leaching with $(\text{NH}_4)_2\text{SO}_4$ solution has also revealed serious environmental problems, such as ammonia-nitrogen pollution in water body and plant growth difficulties (Yang et al., 2013). High ammonium sulfate contaminations in both groundwater (3500–4000 mg/L) and surface water (80–160 mg/L) with

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elevated pH have been reported (Liu, 2002), and it will lead to water eutrophication and stream biodiversity decline. In addition, capillary forces surrounding the leaching holes attract high concentrations of $(\text{NH}_4)_2\text{SO}_4$ back to the topsoil layer, destroying surface vegetation and plants and making rehabilitation more difficult (Li et al., 2010). Therefore, it is necessary to look for a more environmentally friendly leaching agent to replace the existing system.

According to several reports, the soil of southern China is in need of magnesium fertilizer due to the lack of ion-exchangeable magnesium (Bai et al., 2004). Moreover, based on the fact that there is low magnesium content and low demand of magnesium content (hardness) in the underground water and surface water (China Ministry of Environmental Protection, 1993, 2002, 2006), our lab proposes a new technology (Huang et al., 2010) that provides the recovery of rare earths from weathered crust elution-deposited rare earth ore with magnesium salt system. With this new technology, ammonia-nitrogen emissions can be reduced or even eliminated from the source, and may be environmentally friendly to water and mine. In this work, magnesium sulfate had been used individually to be the leaching agent in the recovery process of the weathered crust elution-deposited rare earth ore in columns. Experimental work was conducted to investigate the influence of magnesium sulfate concentration, temperature, pH, and flow rate on rare earth leaching efficiency. The leaching kinetics had been studied as well in order to know the mechanism of rare earth leaching. Furthermore, the residual amount of magnesium in tailings after leaching and washing processes was studied to evaluate the influence of magnesium on the mine. Overall, this provided a theoretical basis and scientific approach to achieve high efficiency and optimized leaching conditions in industrial practice, and developed more evidence and better understanding of the magnesium sulfate as a productive leaching agent.

2. Experimental

2.1. The characterization and composition of experimental rare earth ore

The experimental samples of weathered crust elution-deposited rare earth ores were collected from Liutang Rare Earth Mine area located in the Chongzuo City, Guangxi Province, China. The chemical composition of ore sample was listed in Table 1, which was determined by X-ray Fluorescence (SHIMADZU Co., Ltd. Japan) The rare earth content in Table 1 represented the content of the ion-exchangeable phase rare earth, and the partitioning of the ion-exchangeable phase rare earth was shown in Table 2. They were analyzed by National Tungsten & Rare-earth Product Quality Supervision Testing Center, Ganzhou, China and determined by titration with EDTA and ICP-AES (VARIAN, 720-ES), respectively. The rare earth ore was middle yttrium and contained only 0.15% rare earths.

2.2. Column leaching tests

Columns of 40 mm inner diameter with a heating jacket were used as the apparatus in this test, and precision pumps (Baoding Longer Precision Pump Co., Ltd, BT100-1F) were used to control the flow rate of the leaching agent. And the water bath (Shanghai Sunny Hengping Scientific Instrument Co., Ltd, DC-0506) was used to provide circulating water to maintain the temperature for both leaching agent and column. The schematic plot of apparatus was shown in Fig. 1. All chemicals used in the experiments were of analytical grade.

Table 1
The main chemical composition of Congzuo rare earth ore sample (mass fraction %).

Element	RE ₂ O ₃	MgO	Al ₂ O ₃	CaO	SiO ₂	Fe ₂ O ₃	Na ₂ O	K ₂ O
Content	0.15	0.22	21.93	0.08	66.64	5.96	0.15	3.80

Table 2

The partitioning of the ion-exchangeable phase in the Congzuo rare earth ore (mass fraction %).

Element	La ₂ O ₃	CeO ₂	Pr ₆ O ₁₁	Nd ₂ O ₃	Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃	Tb ₄ O ₇
Content	21.87	2.99	5.32	18.68	3.98	0.68	4.57	0.78
Element	Dy ₂ O ₃	Ho ₂ O ₃	Er ₂ O ₃	Tm ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	Y ₂ O ₃	
Content	4.43	0.88	2.36	0.29	1.51	0.20	31.46	

In the leaching process, 300 g of dried rare earth ore in a specific particle size, obtained by the method of quadrate, was packed into the column, and slightly tapped on the column to make the packed bed height of 20 cm. The column with ore was eluted with the leaching agent of a given concentration and pH at a desired leach flow rate in a specified temperature. Leaching solution samples (25 mL) were collected from the bottom of column, and the rare earth concentration was analyzed by ICP-AES (PerkinElmer, Co., LTD. Optima 8300). From the analysis results the rare earth leached efficiency (η) was calculated according to the following equation:

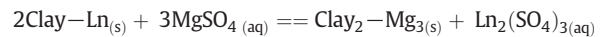
$$\eta = \varepsilon_V / \varepsilon_0 \text{ OR } \eta = \varepsilon_t / \varepsilon_0 \quad (1)$$

where: ε_V was the total amount of rare earth in the leaching solution before the collected volume was V , ε_t was the total amount of rare earth in the leaching solution before the leaching time was t , and ε_0 was the total amount of the ion-exchangeable phase rare earth in the original ore sample.

3. Results and discussion

3.1. Leaching mechanism for rare earth

Clay mineral could absorb rare earth ions because of its negative charge, forming weathered crust elution-deposited rare earth ore. The absorbed REEs could easily and selectively be desorbed and substituted on the substrate by the cations and transferred into the solution as soluble REE sulfates (Moldoveanu and Papangelakis, 2012). The leaching reactions of the ion-exchangeable rare earths in the ore with magnesium sulfate are as following:



where: s and aq represent the solid phase and aqueous phase respectively. It shows that the clay minerals with adsorbed rare earth can be seen as a special inorganic ion exchange resin. The leaching process can be described as the desorption process or ion-exchange process of rare earth. However, rare earths are adsorbed on clay mineral by electrostatic interaction, and the rate of chemical exchange reaction is much faster than the diffusion rate (Jiang et al., 1992; Agbenin and

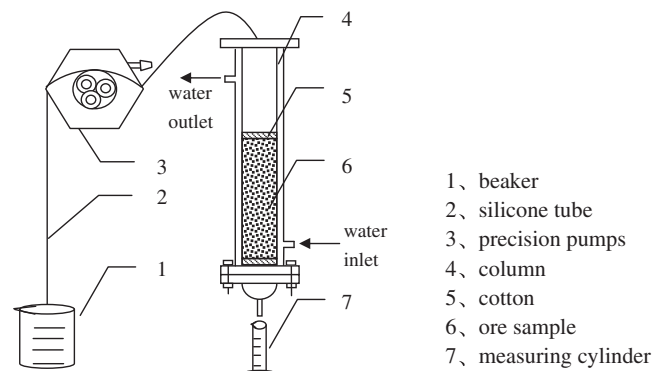


Fig. 1. The schematic plot of apparatus used in this test.

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