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Role of minerals properties on leaching process of weathered crust elution-deposited rare earth ore

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Abstract: Granite belonged to intrusive rock and volcanic was extrusive rock. There may be many differences in their degree of weathering and mineral chemical composition. The present study investigated the minerals properties and the leaching mechanism of the granitic weathered crust elution-deposited rare earth ore from Longnan Rare Earth Mine area (LN ores) and volcanic weathered crust elution-deposited rare earth ore from Liutang Rare Earth Mine area (LT ores). The X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) were used to characterize the phase of rare earth ores. The particle size distributions and main composition of the ore were also presented in this paper. The leaching mechanisms of two kinds of rare earth ores were analyzed with different kinetics models and could be described by the shrinking-core model. They were all inner diffusion-controlled leaching processes. The leaching equation of the kinetics of the LN ores could be expressed as: $1-\frac{2}{3}\eta_{LN}-(1-\eta_{LN})^{2/3}=0.106r_0^{-0.377}e^{-\frac{1.096\times10^4}{8.314T}}t$, leaching equation of kinetics of LT ores was $1-\frac{2}{3}\eta_{LT}-(1-\eta_{LT})^{2/3}=8.33\times10^{-3}r_0^{-0.411}e^{-\frac{4.640\times10^3}{8.314T}}t$.

The rare earth leaching rate of LT ores was always lower in the same condition, and it would need more time and more $(NH_4)_2SO_4$ consumption to achieve the same rare earth leaching efficiency, which would lead to more serious ammonia-nitrogen pollution. Therefore, magnesium salt was proposed as the leaching agent to eliminate ammonia-nitrogen pollution and further studies would be taken in the future.

Keywords: rare earths; leaching; granitic; volcanic; elution-deposited

Rare earth elements (REEs) comprise of 15 lanthanides, scandium and yttrium. They have become vital and indispensable components of many high-tech products, devices and technologies, including clean energy, national security systems, and military and defense applications, especially for the mid and heavy rare earth elements[1–3]. China's rare earth reserves which are of industrial grade are predominantly in three categories: mixed bastnaesite and monazite, bastnaesite and the weathered crust elution-deposited rare earth ore[4]. There are many advantages of the weathered crust elution-deposited rare earth ore, such as widespread distribution of rich reserves, low radioactivity, and it is rich in the middle and heavy rare earth elements and is the main resources of mid and heavy rare earth in the world[5–7]. The metallogenetic mechanism of this kind of ore could be that: granite or volcanic rocks were weathered in humid and warm climate, being transformed into clay minerals such as kaolinite, halloysite and montmorillonite[8]. And the rare earth minerals were also weathered and rare earth ions were released into aqueous phase. Then rare earth ions were absorbed by clay minerals with the migrating flow of natural water[9]. Conventional physical processing methods were found to be useless in the enrichment of rare earths from such sources, but the rare earths can be leached when encountering the cations (Na^+, Mg^{2+}, H^+, and NH_4^+)[10,11].

Since the weathered crust elution-deposited rare earth ores in China were discovered in 1969, the scientists and engineers have been engaged in the development of a series of hydrometallurgy for the special weathered crust elution-deposited rare earth ores[12], such as pool leaching, dump leaching and the *in-situ* leaching process with $(NH_4)_2SO_4$ solution. Recently, new findings were focused on the intensification leaching and the impurities inhibited leaching[13,14]. However, the objects in these researches were mostly granitic weathered crust elution-deposited rare earth ore, and there were few reports about the leaching characteristics of volcanic weathered crust elution-deposited rare earth ore. It was an important part of weathered crust elution-deposited rare earth ore and was

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9% of the rare earth reserves in the Nanling region[8]. Furthermore, granite and volcanic rocks all are the acid rock, but granite belongs to intrusive rock and volcanic is extrusive rock[15], as shown in Fig. 1, there are differences in the degree of crystallization and mineral chemical composition[15]. So the development condition of the weathering crust, the degree of weathering and mineral chemical composition of these ores may be different because of the differences of the protolith and weather conditions[8,16–18]. What's more, a great deal of volcanic weathering crust elution-deposited ore has been found in Guangxi province recently. Therefore, it is necessary to study the comparison in the minerals properties and the leaching characteristics between granitic and volcanic weathered crust elution-deposited rare earth ore for the better application of volcanic weathering crust elution-deposited ore.

In this paper, the physicochemical property and the column leaching kinetics between the granitic weathered crust elution-deposited rare earth ore from Longnan Rare Earth Mine area (LN ores) and volcanic weathered crust elution-deposited rare earth ore Liutang Rare Earth Mine area (LT ores) were investigated. It would be useful to provide a reasonable explanation to actual situation and a theoretic basis for leaching rare earth from these ores.

1 Experimental

1.1 Preparation and analysis of the weathered crust elution-deposited rare earth ores

Two kinds of rare earth ores known as granitic weathered crust elution-deposited rare earth ore from Longnan Rare Earth Mine area located in the Ganzhou City and volcanic weathered crust elution-deposited rare earth ore from Liutang Rare Earth Mine area located in the Chongzuo City were employed in the present work, and referred to as LN ore and LT ore respectively. The X-ray diffraction patterns for ores were recorded by an X'Pert PRO MPD X-ray diffractometer (PANalytical Co., Ltd., Netherlands) using Cu Kα. The chemical composition of ore samples was determined by X-ray fluorescence (SHIMADZU Co., Ltd., Japan). The partitioning of the ion-exchangeable phase from the two kinds of rare earth ores was determined by National Tungsten & Rare-earth Product Quality Supervision Testing Center, Ganzhou, China with ICP-AES (VARIAN, 720-ES). The particle size distributions were obtained by the standard sieve of China. FT-IR spectra were taken by a Magna-IR 750 Fourier transform infrared spectrometer (Nicolet Co., Ltd., USA) in the range of 400–4000 cm^{-1}.

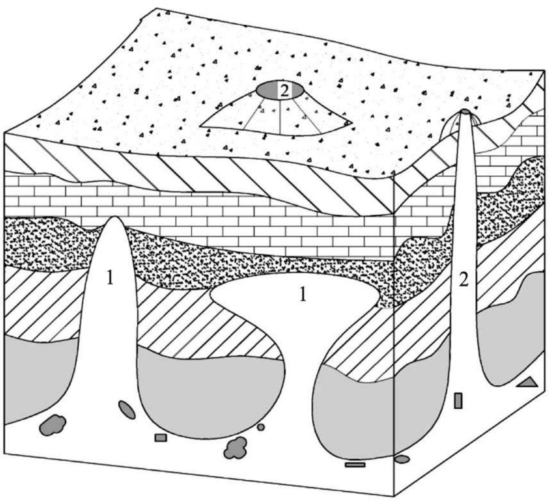

Fig. 1 Schematic plot of the forming process of rock[15]

1. Intrusive rock—protolith of granitic weathered crust elution-deposited rare earth ore; 2. Extrusive rock—protolith of volcanic weathered crust elution-deposited rare earth ore

1.2 Apparatus and experimental procedure

In the present work, deionized water and analytical grade ammonium sulfate were used. Columns of 40 mm inner diameter (made by Beijing Organic Glass Products Factory) was employed as the apparatus and peristaltic pump (Baoding Longer Precision Pump Co., Ltd., BT100-1F) were used to control the flow rate of leaching agent, as is shown in Fig. 2.

In the column leaching process, 300 g dried rare earth ore in a specific particle size, obtained by the method of quadrate, was packed into the column, and slightly taped on the column to make the packed bed height consistent. The column was eluted with 0.20 mol/L $(NH_4)_2SO_4$ at a flow rate of 0.60 mL/min in a specified temperature. Leaching solution samples (12.5 mL or 25 mL) were collected from the bottom of column and the rare earth concentration was analyzed by ICP-AES (Perkin Elmer, Co., Ltd., Optima 8300). The leaching process was evaluated by the RE leaching efficiency, which was calculated according to the following formula:

$$\eta=\varepsilon_t/\varepsilon_0 \quad (1)$$

where: ε_t was the total amount of rare earth in the leaching solution before the leaching time was t and ε_0 is the total amount of rare earth present in the original ore sample.

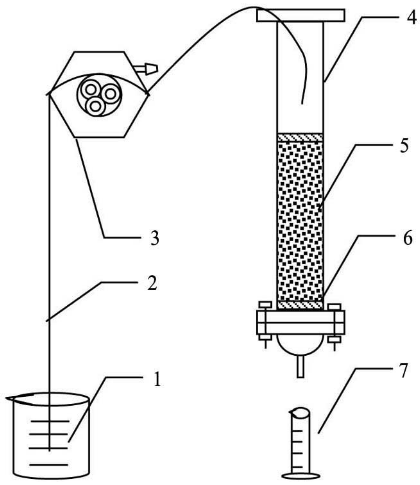

Fig. 2 Schematic plot of apparatus used in this test

1–Beaker; 2–Silicone tube; 3–Peristaltic pump; 4–Column; 5–Ore sample; 6–Cotton; 7–Measuring cylinder