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Mineral properties and leaching characteristics of volcanic weathered crust elution-deposited rare earth ore

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Abstract: Weathered crust elution-deposited rare earth ore is an important resource of rare earths, including grantic weathered crust elution-deposited rare earth ore and volcanic weathered crust elution-deposited rare earth ore. The development condition of the weathered crust, weathering degree and mineral composition of these ores will be different because of the differences between their parent rocks and weathered crust causes of mineralogy path. Therefore, mineral properties and leaching characteristics of volcanic weathered crust elution-deposited rare earth ore from Chongzuo (CZ), Guangxi province were investigated. It was found that the CZ rare earth ore was a typical mid-yttrium and rich-europium ore, with the overall rare earth (REE) grade in ion-exchangeable phase of 0.15%. Partide size classification showed that finer particle had a higher REE grade. Column leaching tests showed that the leaching efficiency of REE was above 94% with leaching agent concentration of 0.20 mol/L, liquid-solid ratio of 4:3, flow rate of 0.60 mL/min, and initial pH value around 5.67. Compared to ammonium sulfate leaching, magnesium sulfate leaching was advantaged by nearly zero ammonia nitrogen emission while their REE leaching was almost equivalent.

Keywords: rare earth; volcanic; weathered crust; ammonium sulfate leaching; magnesium sulfate leaching

Over the past two decades, with the breakthroughs of the application research of rare earth in the field of high-tech area, the national strategic status of rare earth elements (REE) is growing. REE have become indispensable elements in the new materials industry, especially the middle and heavy REE (M-HRE). Over 80% of the world's total M-HRE reserves exists in the weathered crust elution-deposited rare earths ore in China[1,2]. It is mainly distributed in southern provinces of China, such as Jiangxi, Guangxi, Guangdong, Fujian, Hunan provinces[3]. In recent decades, three leaching technologies in industry, i.e. the sodium chloride pool leaching, ammonium sulfate pool leaching and ammonium sulfate *in situ* leaching[4], have been successfully developed.

Weathered crust elution-deposited rare earth ores mainly divide into grantic weathered crust elution-deposited ore and volcanic weathered crust elution-deposited ore according to their parent rocks. Granite belonged to intrusive rock while volcanic was extrusive rock, there may be many differences in their weathering degree and mineral composition[5]. Grantic weathered crust elution-deposited rare earth ore accounts for 54% of the total reserves in Nanling region of China, while volcanic weathered crust elution-deposited rare earth ore accounts for 9%[6]. Recently, a large quantity of volcanic weathered rare earth ore has been found in Guangxi province. However, most of the previous study focus on the grantic weathered crust elution-deposited ore. And the theoretical research mainly contain impurities inhibition leaching[7–8], compound leaching[9–11] and enhanced leaching[12–15]. Due to the difference between their parent rocks, the weathering process and weathering degree of the protolith is different, resulting in a difference in the particle size, mineral composition and crystallinity. As a consequence, their mineral properties and leaching characteristics may be different, so it is of great necessity and significance to investigate volcanic weathered crust elution-deposited rare earth ore.

1 Experimental

1.1 Preparation and analyses of ore sample

The volcanic weathered crust elution-deposited rare earth ore employed in the experiment was collected from Liutang rare earth mine in Chongzuo (CZ), Guangxi province, and its parent rock is intermediate-acid volcanics. The rare earth elements absorbed on the clay minerals in the form of ion phase oxide. X-ray fluorescence

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(XRF, ZSX Primus II) was employed to determine the overall chemical composition of ore sample; the grade of REE in the ion-exchangeable phase of the ore sample was determined by National Tungsten & Rare-earth Product Quality Supervision Testing Center with ICP-AES (VARIAN, 720-ES) in Ganzhou, China. X-ray diffraction (XRD) was used to gain additional quantitative information about the nature of ore sample.

1.2 Column leaching tests

Deionized water and $(NH_4)_2SO_4$ with analytical grade were used in the present work. Column leaching experiment was conducted under ambient temperature (25 ºC) in columns with inner diameter of 45 mm. During column leaching, 300 g ore was added into the columns and the columns were patted slightly to make the height of the ore bed to be 20 cm, the flow rate of leaching agent ($(NH_4)_2SO_4$) was controlled by precision pumps (Baoding Longer Precision Pump Co., Ltd., BT100-1F). The ore bed was eluted with leaching agent with given concentration and pH, and leaching solution samples (25 mL) were collected from the bottom of column. The concentration of REE in the leaching solution was determined by ICP-AES (Perkin Elmer, Co., Ltd. Optima8300).

To evaluate the leaching process, the leaching efficiency of REE (η) was the crucial parameter, which was calculated by the following equation:

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

where ε_V is the total amount of rare earth in the leaching solution when the collected volume is V, ε_0 is the total amount of rare earth in the original ore sample.

2 Results and discussion

2.1 Characterization of volcanic ore

The crystal structure of ore samples was analyzed by X-ray powder diffraction, as shown in Fig. 1. The volcanic ore is mainly consisted of clay minerals (such as kaoline), quartz sand, and rock-forming feldspar. Chemical composition of the volcanic ore is shown in Table 1, SiO_2, Al_2O_3, Fe_2O_3, and K_2O were found to be

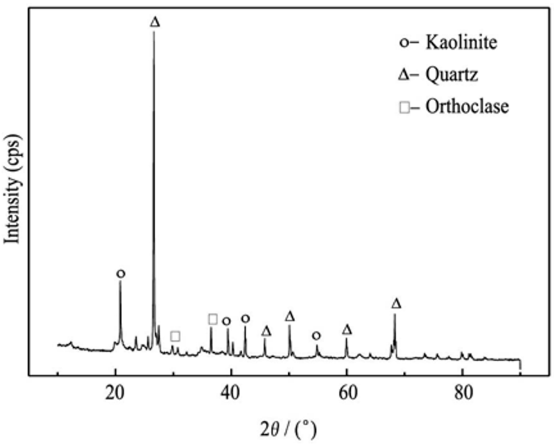

Fig. 1 XRD pattern of CZ rare earth ore sample

Table 1 Chemical composition of CZ rare earth ore sample (wt.%)

REO	MgO	Al_2O_3	CaO	SiO_2	Fe_2O_3	Na_2O	K_2O
0.15	0.22	21.93	0.08	66.64	5.96	0.15	3.77

Table 2 Chemical composition of rare earth element in CZ rare earths ore sample (wt.%)

La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7
21.87	2.99	5.32	18.68	3.98	0.68	4.57	0.78
Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3	REO
4.43	0.88	2.36	0.29	1.51	0.20	31.46	100

the major compounds, and the total REE content in ion-exchangeable phase was 0.15 wt.%. REE partitioning of the ore sample (Table 2) indicated that the CZ rare earth ore was a typical mid-yttrium and rich-europium ore. Particle size distribution and the relevant REE grade in ion-exchangeable phase of CZ rare earth ore sample are shown in Fig. 2. It can be seen that the ore sample had a wide size distribution and the particle size of above 37% of the ore sample is lower than 0.15 mm. REE grade in ion-exchangeable phase increased with the decrease of the particle size.

2.2 Column leaching process

2.2.1 Influence of leaching agent concentration

Leaching agent concentration is an important factor affecting the leaching process. The function of the leaching agent is to recover the REE adsorbed on ores which is dominated by law of mass action via an ion-exchange mechanism. The column leaching was conducted under the conditions of temperature (T) 25 ºC, flow rate (v) 0.60 mL/min, leaching agent with initial pH value 5.67, moisture content (M) 0%, and the leaching agent concentration varied from 0.5 to 0.3 mol/L. The results are presented in Fig. 3.

It can be seen that the leaching efficiency of REE increased from 70% to 98% with the increase of the leaching agent concentration. This may be due to the fact that higher NH_4^+ concentration induces the ion-exchange re-

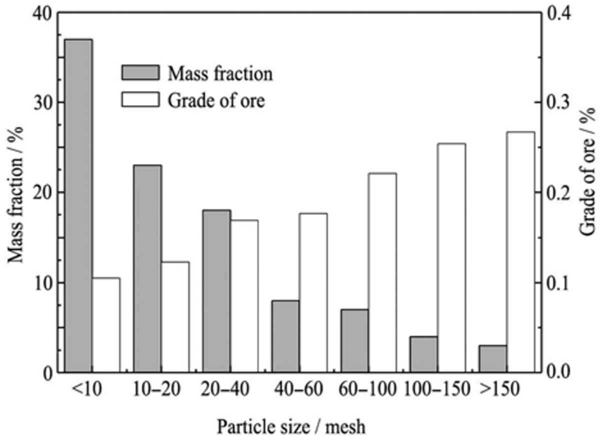

Fig. 2 Particle size distribution and relevant REE grade of CZ rare earth ore sample