

## Adsorption ability of rare earth elements on clay minerals and its practical performance

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**Abstract:** The adsorption behaviors of rare earth elements on clay minerals would have great influence on the mineralization process and the leaching process of the ion-adsorption type rare earths ore. In this work, the adsorption thermodynamics of REEs on kaolin were investigated thoroughly and systematically. The experimental results showed that the adsorption characteristics of La, Nd, Y on kaolin did fit well with the Langmuir isotherm model and their saturated adsorption capacities were 1.731, 1.587 and 0.971 mg/g, respectively. The free energy change ( $\Delta G$ ) values were  $-16.91$  kJ/mol (La),  $-16.05$  kJ/mol (Nd) and  $-15.58$  kJ/mol (Y), respectively. The negative values of  $\Delta G$  demonstrated that the adsorption of rare earth on kaolin was a spontaneously physisorption process. The deposit characteristic of the volcanic ion-adsorption type rare earths ore and the behavior of the rare earth in the column leaching process were also developed here. With the increase of the ore body depth, the distribution of the LREEs decreased and the HREEs increased. And the slight differences in the adsorption ability of REEs on clay minerals led to the fractionation effect in the column leaching process. These developed more evidences and better understanding of metallogenic regularity, and provided a theoretical basis and scientific approach to separation of the HREEs and LREEs in the leaching process.

**Keywords:** rare earth; adsorption ability; deposit characteristics; column leaching

“Rare earths” (RE) refer to the 15 elements of the periodic table known as “lanthanides” with yttrium and scandium, and the rare earth elements are usually divided into three categories except Pm and Sc. Light rare earth elements (LREEs) refer to La, Ce, Pr and Nd. Middle rare earth elements (MREEs) refer to Sm, Eu and Gd. Heavy rare earth elements (HREEs), refer to the rest of lanthanides elements and yttrium<sup>[1]</sup>. The ion-adsorption type rare earths ore, is mainly located in China, especially in Jingxi, Fujian, Hunan, Guangdong, Yunnan and Guangxi provinces. The ore has many advantages, such as complete rare earth partition, low radioactivity, and rich in the MREEs and HREEs<sup>[2]</sup>. It is the main resources of MREEs and HREEs in the world. The metallogenetic mechanism of the ore could be as follows<sup>[3]</sup>: The granite or volcanic rocks are weathered in the humid and warm climate, and transform into clay minerals such as kaolin, halloysite and montmorillonite. The rare earth minerals are also weathered to be rare earth ions. When the rare earth ions travel with the migration of natural water, they would be absorbed by clay minerals and present as the ion-exchangeable phase rare earths. Finally, the ion-adsorption type rare earths ore forms. Conventional

physical processing methods are found to be useless in the enrichment of rare earths from such sources. But the ion-exchangeable phase rare earths can be leached when encountering the cations ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ , and  $\text{NH}_4^+$ )<sup>[4]</sup>. It is thus evident that the adsorption behavior of rare earth elements on clay minerals would have great influence on the mineralization process and the leaching process of the ion-adsorption type rare earths ore.

Nowadays, there are a lot of researches carried out by agrologists and geologists on the adsorption and desorption of rare earth elements with clay minerals, such as the factor studies with various soils and different environmental conditions<sup>[5,6]</sup>, as well as the mechanism study<sup>[7,8]</sup>. They were developed in order to study the geochemical characteristics<sup>[9,10]</sup>, the environmental pollution and agricultural application of rare earth elements<sup>[11,12]</sup>. This paper was written from the perspective of metallurgy and mineralogy. La, Nd and Y were chosen as research objects owing to their high partition in the ion-adsorption type rare earths ore, and kaolin was chosen as the representative of the clay minerals. Equilibrium adsorption experiments were taken to acquire the saturated adsorption capacity and the Gibbs free energy change by static

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adsorption method, which could determine the adsorption ability of rare earth elements (REEs). Then, based on the studies above, the deposit characteristic of the volcanic ion-adsorption type rare earths ore, located in the Chongzuo City, Guangxi Province, was studied by a soak leaching method. The behavior of the rare earths in the column leaching process was also investigated in this paper. Overall, this work obtained more evidences and better understanding of metallogenic regularity, thus providing a theoretical basis and scientific approach for the separation of HREEs and LREEs in the leaching process.

## 1 Experimental

### 1.1 Raw material and reagent

All chemicals used in the experiments such as ammonium sulfate, magnesium sulfate, kaolin, hydrochloric acid, and so on were of chemical purity.

In the equilibrium adsorption experiments, lanthanum chloride solution was prepared by dissolving its carbonate (>99.9%, Guosheng Rare Earth Co., Ltd., Jiangsu) in HCl solution, so did the neodymium chloride solution and yttrium chloride solution. The study of deposit characteristics was carried out by the soak leaching process; its experimental samples were the volcanic ion-adsorption type rare earths ore of completely weathering layer in different depths, collected by deep drilling boreholes. They were from Liutang (LT) Rare Earth Mine area located in the Chongzuo City, Guangxi Province, China. In the column leaching process, the ion-adsorption type rare earths ore samples were collected from LT area, too. The content and the partitioning of ion-exchangeable phase rare earth of these samples are shown in literature<sup>[13,14]</sup>.

### 1.2 Apparatus and experimental procedure

In the equilibrium adsorption experiments, 40 mL rare earth chloride solution in pH 4.80 with a certain concentration was acquired and poured into the conical flask. And  $1.0000 \pm 0.0020$  g kaolin was also added into the conical flask to take an adsorption process in the constant temperature oscillator. The adsorption equilibrium could be achieved after 30 min oscillation at 25 °C, according to the time-dependent experiments. Then the mixture in the conical flask underwent a solid-liquid separation process by centrifugation. The concentrations of the rare earth ions before and after equilibrium were measured by ICP-AES (PerkinElmer, Co., Ltd., Optima 8300). Each experiment was repeated thrice. The equilibrium adsorption capacity  $Q_e$  (mg/g) was calculated by:

$$Q_e = 0.04 \times (C_0 - C_e) / m \quad (1)$$

where  $C_0$  is the initial concentration of RE in rare earth chloride solution, mg/L;  $C_e$  the equilibrium concentration of RE in the solution after adsorption, mg/L;  $m$  the mass of kaolin, g;  $Q_e$  the equilibrium adsorption capacity,

mg/g.

In the soak leaching process, 200 g dried rare earths ore in different depths with an average particle size of 1.0 mm was obtained by the method of quadrating, and it was put into a 400 mL beaker. 250 mL 5% ammonium sulfate solution in natural pH was also put in the beaker to take a soak leaching experiment. The leaching temperature was 25 °C and the leaching time was 12 h, and there was a stir once every 2 h in the leaching process. The beaker was covered by plastic film to prevent moisture loss. After the leaching process, the leaching liquor was achieved with vacuum suction filter for solid-liquid separation and was finally diluted to 500 mL. The rare earth concentration and partitioning of the leaching liquor were analyzed by ICP-AES. The total rare earth in the 500 mL leaching liquor was the total amount of ion-exchangeable phase rare earth in the ore sample.

In the column leaching process, columns of 40 mm inner diameter were used as the apparatus, and precision pumps (Baoding Longer Precision Pump Co., Ltd., BT100-1F) were used to control the flow rate of leaching agent. 300 g dried rare earths ore in an average particle size of 1.0 mm, 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 magnesium sulfate leaching agent in natural pH, at a flow rate of 0.60 mL/min, at 298 K. Leaching liquor samples (25 mL) were collected from the bottom of column and the rare earth concentration and partitioning of the leaching liquor were analyzed by ICP-AES as well.

## 2 Results and discussion

### 2.1 Adsorption thermodynamics

#### 2.1.1 Adsorption equilibrium

Adsorption isotherms are important for the description how molecules or ions of adsorbate interact with adsorbent surface sites. In the present study, in order to study the thermodynamics of RE adsorption on kaolin, La, Nd and Y elements were chosen as adsorbate because of its high partition in the ion-adsorption type rare earths ore. The equilibrium adsorption experiments were conducted with seven different initial concentrations. They were 10, 30, 50, 70, 100, 120, 150 mg/L for La and Nd, and 10, 20, 30, 50, 70, 90, 120 mg/L for Y. The adsorption isotherms are shown in Fig. 1. It is shown in Fig. 1 that the adsorption regularity of rare earth elements was consistent. The equilibrium adsorption capacity would increase firstly and then became relatively stable with the increase of equilibrium concentration. In order to gain a better understanding of the mechanism and to quantify the adsorption data, Langmuir and Freundlich models were used to fit the adsorption isotherm and to simulate the experimental data.

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