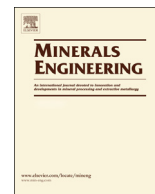




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Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

A discussion on the leaching process of the ion-adsorption type rare earth ore with the electrical double layer model



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ARTICLE INFO

Keywords:

Electrical double layer model

Rare earth

Adsorption

Ammonia-nitrogen emissions

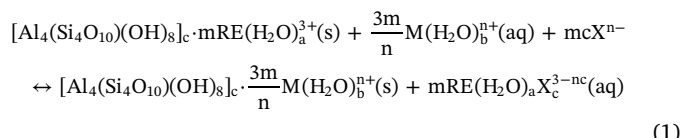
ABSTRACT

The practice of in-situ leaching of the ion-adsorption type rare earth ore using $(\text{NH}_4)_2\text{SO}_4$ had revealed serious ammonia-nitrogen pollution. Therefore, a discussion on the leaching process of the ion-adsorption type rare earth ore with the electrical double layer model was presented in this paper, so as to screen out the green and efficient leaching agent and the appropriate leaching measures to improve the rare earth leaching efficiency and reduce or even eliminate ammonia-nitrogen emissions. It was determined that the leaching process could be described as the formation of a new stable electric double layer (EDL). The potential $\varphi(x)$ with the distance x from clay surface to bulk solution in the diffusion layer was obtained, it showed that the potential $\varphi(x)$ would decrease with the increase of the cationic charge of leaching agent, the leaching temperature and the concentration of leaching agent, leading to a higher rare earth leaching efficiency. The theoretical analysis was verified by soak leaching experiments. The results showed that the law of rare earth leaching efficiency was in agreement with the theoretical analysis. And the rare earths partition in the leaching liquor under different conditions was substantially constant except cerium element. Therefore, the cation and anion of leaching agent should have a large electric density and be environmental friendly, of which magnesium sulfate could be preferred. Moreover, chemical substances, which could form a more stable coordination with rare earth ions, could be used as an assistant to promote the leaching equilibrium to move toward a favorable direction. This paper had provided a theoretical foundation and application basis for the leaching of rare earth from the ion-adsorption type rare earth ore, and show the direction on reducing or even eliminate ammonia-nitrogen emissions.

1. Introduction

Rare earth elements (REEs) comprise of 15 lanthanides, scandium and yttrium. They, especially for the mid and heavy rare earth (Chi and Tian, 2008), have become indispensable components of many high-tech products, devices and technologies. The ion-adsorption type rare earth ore, mainly located in China, especially in Jiangxi, Fujian, Hunan, Guangdong, Yunnan and Guangxi provinces, are the main resources of mid-heavy rare earth in the world (Xiao et al., 2015a). It is generally accepted that rare earth (RE) in the ion-adsorption type rare earth ore mainly exists in four phases (Chi et al., 2005): water-soluble phase, ion-exchangeable phase, colloidal sediment phase and minerals phase. The ion-exchangeable phase rare earth is adsorbed on clay minerals, accounting for more than 80% of total RE. Conventional physical processing methods, such as flotation, magnetic, gravity and electrostatic separation, are found to be ineffective in the recovery of rare earths

from this kind of ore (Chi and Tian, 2008). But the adsorbed rare earths can be desorbed when encountering active cations (for example, Na^+ , NH_4^+ and Mg^{2+}). The leaching process of the ore is a kind of ion-exchangeable process between the positive ions in leaching agent and rare earth ions adsorbed on clay minerals (Tian et al., 2013). The chemical reaction equation is as follows:



where a , b , c , m , n represent for integer values, M and X represent for the cation and anion of leaching agent respectively.

This kind of ore has many advantages, such as complete rare earth partition, low radioactivity, simple leaching process and rich in the

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middle and heavy rare earth elements, which makes it a valuable strategic mineral resource. Nowadays, the ion-exchangeable phase rare earth is recovered by in-situ leaching process with $(\text{NH}_4)_2\text{SO}_4$ leaching agent in the industry. One ton of rare earth concentrate production consumes 7–9 tons of ammonium sulfate (Xiao et al., 2015b). High ammonium sulfate contaminations in both groundwater (3500–4000 mg/L) and surface water (80–160 mg/L) have been reported (Liu, 2002). It will lead to water eutrophication and stream biodiversity decline (Yang et al., 2013). Therefore, new studies had been taken recently in order to reduce or even eliminate ammonia-nitrogen emissions (Xiao et al., 2015c). Firstly, kinetics (Tian et al., 2010a; Xiao et al., 2015d) and mass transfer (Tian et al., 2010b) on leaching rare earth from the ion-adsorption type rare earth ore had been investigated. It showed that the leaching process was a reversible and a typical noncatalytic heterogeneous reaction in solid–liquid systems, controlled by inner diffusion model (Xiao et al., 2015d). The leaching efficiency of rare earth increased rapidly in the first 250s which indicated that rare earth leaching behavior was controlled by kinetics at this time. Then the leaching rate slowed down and achieved a leaching equilibrium in 20mins, suggesting that the leaching process approach to a thermodynamic control (Xiao et al., 2015d). Moreover, the leaching behaviors of the single rare earth element was brought into correspondence with rare earths, and their leaching process could be described with inner diffusion control model too (Xiao et al., 2015d). However, these researches only revealed the behavior of the rare earth in the leaching process and provided ideas for the increase of rare earth leaching rate, they did not identify the leaching mechanism and could not acquire the leaching equilibrium law. Secondly, fulvic acid (Luo et al., 2015), carboxymethyl sesbania gum (Tian et al., 2013) and citrate (Li et al., 2015) were used as assistants to achieve a higher rare earth leaching efficiency and reduce the dosage of $(\text{NH}_4)_2\text{SO}_4$. Finally, new non-ammonium leaching agent, such as iron sulfate, aluminum sulfate (Wang et al., 2013), ammonium citrate (Chi et al., 2013), magnesium sulfate (Xiao et al., 2015e), etc., were developed to replace $(\text{NH}_4)_2\text{SO}_4$ to eliminate ammonia-nitrogen emissions. However, the above research works on assistants and new leaching agents only gave a method to reduce or even eliminate ammonia-nitrogen emissions. They did not explain how to choose a leaching agent and which measures can promote the leaching equilibrium to move toward a favorable direction from the perspective of leaching mechanism and reaction equilibrium.

Therefore, based on the principle of cation adsorption by clay mineral, combined with the electric double layer model, a discussion on the leaching process of the ion-adsorption type rare earth ore was presented in this paper. The choices of new leaching agents and the measures which can promote the rare earth leaching efficiency, were systematically analyzed based on the leaching mechanism and reaction equilibrium. Moreover, the verification of the theoretical model was studied with the soak leaching process. This will provide a theoretical foundation and application basis for the leaching of rare earth from the ion-adsorption type rare earth ore, and show the direction on reducing or even eliminate ammonia-nitrogen emissions, This is very important for the efficient exploitation and its sustainable development of the ion-adsorption type rare earth ore.

2. Experimental

2.1. The characterization and composition of experimental rare earth ore

The ion-adsorption type rare earths used in the experiments was collected from 8 to 10 m depth in Liutang (LT) Mine area, in Chongzuo City, Guangxi province. The ore was chosen as representative sample to represent the rare earth ore in completely weathered layer. The ore was dried in drying oven at 50 °C and the ore samples were obtained from the dried ore by the method of quartering. The existing state of rare earth in the LT rare earth ore was determined by the sequential fractionating extraction methods (Chi et al., 2005), the result was

Table 1
Rare earth content in different phases for LT ore sample (wt.%).

Phases	All	Water soluble	Ion-exchangeable	Colloidal sediment	Minerals
Content	1.80	Negligible	1.50	0.14	0.16

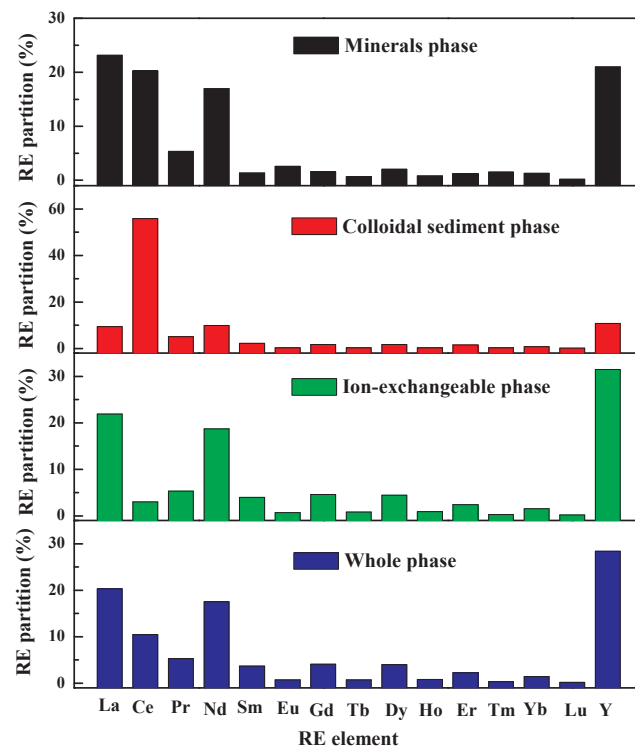


Fig. 1. Rare earths partition in different phases for LT ore sample.

shown in Table 1. Rare earth in the ion-adsorption type rare earth ore presented in four phases: water soluble phase, ion-exchangeable phase, colloidal sediment phase and minerals phase. Water soluble phase rare earth referred to the rare earth dissolved in water, which accounted for less than one in ten thousand of total rare earth and could be negligible. The content of total rare earth was 1.8 wt%. The ion-exchangeable phase rare earth accounted for 83.33% of total rare earth and its content was 1.50 wt%. The colloid sediment and mineral phase accounted for 7.78 wt%, 8.89 wt%, respectively. The rare earths partition in the different state were tested by ICP-AES (PerkinElmer, co., Ltd. Optima 8300) and were shown Fig. 1. According to the rare earths partition in the ion-exchangeable phase, it could be seen easily that the LT ore was a kind of rare earth ore with Middle Y and Rich Eu. Moreover, Ce partition in the ion-exchangeable phase was only 2.99%. Cerium ions were unstable in aqueous or hydroxyl aqueous compound as tetravalent under natural oxidation environment (Chi et al., 2005). They could be easily oxidized and precipitated, forming $\text{CeO}_2/\text{Ce}(\text{OH})_4$, so the cerium deficient phenomenon appeared and the Ce partition was low in ion-exchangeable phase (Chi et al., 2005). In the colloid-sediment phase, cerium existed mainly in the form of $\text{CeO}_2/\text{Ce}(\text{OH})_4$. Therefore, the Ce partition in the colloidal sediment phase could be 55.84%, more than half of total rare earth.

Furthermore, the crystal structure of the ore samples were analyzed by X-ray powder diffraction, shown in Fig. 2. It was visible that there were clay minerals (such as kaoline $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$, quartz (SiO_2) , sanidine $(\text{K}(\text{AlSi}_3\text{O}_8))$) in the rare earth ore. The chemical composition of ore samples were listed in Fig. 3, determined by X-ray Fluorescence (SHIMADZU Co., Ltd. Japan). As seen in Fig. 3, SiO_2 and Al_2O_3 were the main composition of the ore, which was in good with mineral

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