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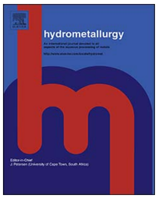

Reduction leaching of rare earth from ion-adsorption type rare earths ore: II. Compound leaching

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ABSTRACT

The colloidal sediment phase rare earth was little leached even if the pH of leaching agent reached 1.00, but part of it could be reduction leaching by the ferrous ion. To solve the problems appeared in the $FeSO_4$ leaching process, a magnesium-ferrous compound leaching was put forward in this paper. It was demonstrated that lower proportion of Mg/Fe and higher acidity of leaching agent, could result in a higher rare earth leaching efficiency and relative a bigger cerium partition in the leaching liquor. But the leaching performance of the magnesium-ferrous compound leaching system was unsatisfactory because of some problems. Therefore, another compound leaching method using $MgSO_4$ and ascorbic acid was proposed, taking advantage of the reducibility and the ability to strengthening the leaching process of ascorbic acid. It was shown that about 50% rare earths colloid sediment phase was dissolved into the leaching liquor when with 0.20 mol/L $MgSO_4$ and 0.5 g/L ascorbic acid. 85.85% rare earth leaching efficiency and a low content of Fe and Al were achieved as well. Therefore, compound leaching with $MgSO_4$ and ascorbic acid was proposed to an excellent alternative leaching agent for further studies, which may realize efficiency extraction, low consumption and be environmentally friendly.

1. Introduction

Rare earth elements (REEs) comprise of 15 lanthanides, scandium and yttrium. They are usually divided into three categories except Pm and Sc (Xu, 2002), light rare earth elements (LREEs), middle rare earth elements (MREEs) and heavy rare earth elements (HREEs). The MREEs and HREEs, which are of vital importance for the hi-tech industry because of their unique properties, are high-priced and in low-supply (Chen, 2011). The ion-adsorption type rare earths ore, first discovered at 1969, are mainly located in the seven provinces of South China. This kind of ore has many advantages, such as complete rare earth partition, low radioactivity, simple leaching process and rich in the middle and heavy rare earth elements, which makes it a valuable strategic mineral resource (Chi and Tian, 2006).

Rare earth in the ion-adsorption type rare earths ore 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 accounts for more than 80% of whole-phase rare earth in general. It can be easily released when encountering the cations (such as $NH_4{}^+$, Mg^{2+}) (Tian et al., 2010). Nowadays, rare earth is recovered with $(NH_4)_2SO_4$ in the industry, and the leaching reaction can be expressed as Eq. (1). The reaction is an ion-exchangeable process between the cations in the leaching agent and the rare earth absorbed on the clay minerals (Chi and Tian, 2006).

$$[Al_4(Si_4O_{10})(OH)_8]_m\cdot nRE^{3+}{}_{(s)} + 3nNH^{+}_{4(aq)} \leftrightarrow [Al_4(Si_4O_{10})(OH)_8]_m\cdot 3nNH^{+}_{4(s)} + nRE^{3+}{}_{(aq)} \qquad \text{Eq. (1)}$$

where: s and aq represent solid phase and aqueous phase, respectively. And m, n represent for Arabic numerals.

Although the $(NH_4)_2SO_4$ leaching agent has been widely used in industrial production, there are still some problems as follows: (1) 7–9 tons $(NH_4)_2SO_4$ consumption was required for every tons of rare earth concentrate, which could lead to a serious ammonia-nitrogen pollution (Xiao et al., 2015a). (2) $(NH_4)_2SO_4$ could desorb most of rare earth in the ion-exchangeable phase, but not the colloidal phase which accounts for above 5% of whole-phase rare earth (Tian et al., 2013). For the first problem, an innovative magnesium salt leaching agent (Xiao et al., 2015b) was proposed by our team to deal with the ion-adsorption type rare earths ore. With the new leaching agent, the problem of ammonia nitrogen pollution could be solved. Moreover, the application of magnesium salt leaching agent could maintain the soil nutrient so as to reduce the dosage of calcium–magnesium fertilizer, and may realize

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the ecological friendly leaching of the ion-adsorption type rare earths ore (Xiao et al., 2016a). Meanwhile, the reduction leaching of rare earth from ion-adsorption type rare earths ore with $FeSO_4$ was put forward to solve the second problem (Xiao et al., 2016b). The column leaching experiments of the ion-adsorption type rare earths ore were carried out in the condition of 0.20 mol/L leaching agent, pH 2.00, a flow rate of 0.6 mL/min, 25 °C. It was shown that the rare earth leaching efficiency with $FeSO_4$ leaching agent was about 85.50%, and it was only 81.58% when with $(NH_4)_2SO_4$ agent (The content of ion-exchangeable phase rare earth was accounted for 83.33% of the whole-phase rare earth in the experimental sample). Moreover, the study of the existing state of rare earth in the leaching residues showed that part of colloidal sediment phase rare earth could be reduction leached by Fe^{2+} and the leaching efficiency was about 50%. However, the use of $FeSO_4$ may bring environmental problems, increase the consumption of impurity removal reagents and the precipitation agent, lead to high costs and low product purity.

In view of the environmental friendly characteristics of $MgSO_4$ and the reduction properties of $FeSO_4$, the magnesium-ferrous compound leaching of rare earth from ion-adsorption type rare earths ore was put forward, it had been taken into consideration to solve problems existed in the $FeSO_4$ leaching process, and to achieve none of ammonia-nitrogen emissions from the source. In this paper, the analysis on the leaching of colloidal sediment phase rare earth was carried out, and the influence of Mg/Fe proportion and pH values of compound leaching agent on rare earths leaching were presented. Moreover, in view of the reduction property and coordination capability with rare earth, the ascorbic acid was chosen as the addition agent, and the compound leaching with $MgSO_4$ and ascorbic acid was simply performed in this paper. Hence, a feasible operation would be provided for the leaching of colloidal sediment phase as well as for realizing efficiency extraction and environmental friendly.

2. Experimental

2.1. The characterization of experimental ion-adsorption type rare earths ore

The experimental ion-adsorption type rare earths ore was from completely weathered layer, obtained from Liutang (LT) Rare Earth Mine area located in the Chongzuo City.

The existing state of rare earth in the LT rare earths ore was determined with the sequential fractionating extraction methods (Chi et al., 2005), the results were shown in Fig. 1. The content of ion-exchangeable phase rare earth was 1.50‰, accounted for 83.33% of the whole-phase rare earth. Moreover, there was 0.14‰ colloid sediment phase and 0.16‰ minerals phase. The rare earth partition of different phase from the LT ore had been determined by ICP-AES (PerkinElmer, Co., Ltd. Optima 8300) and shown in Fig. 2. Rare earth in this ore contained 15 rare earth elements except Pm and Sc. It can be seen from the rare earth partition of the ion-changeable phase in Fig. 2 that the rare earth ore was the type of middle Y and rich Eu, shown in the.

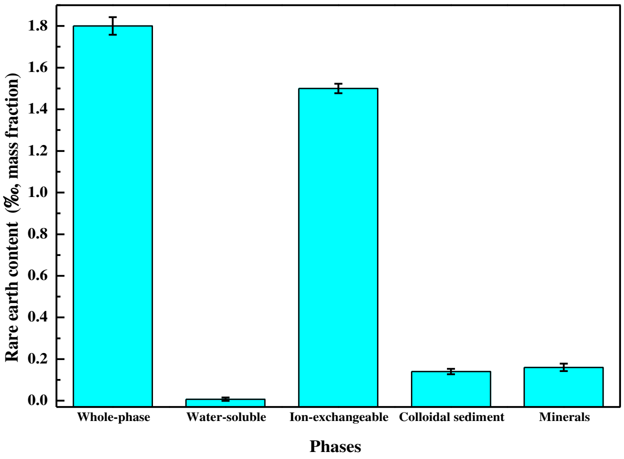

Fig. 1. Rare earth content in different phases for LT ore sample.

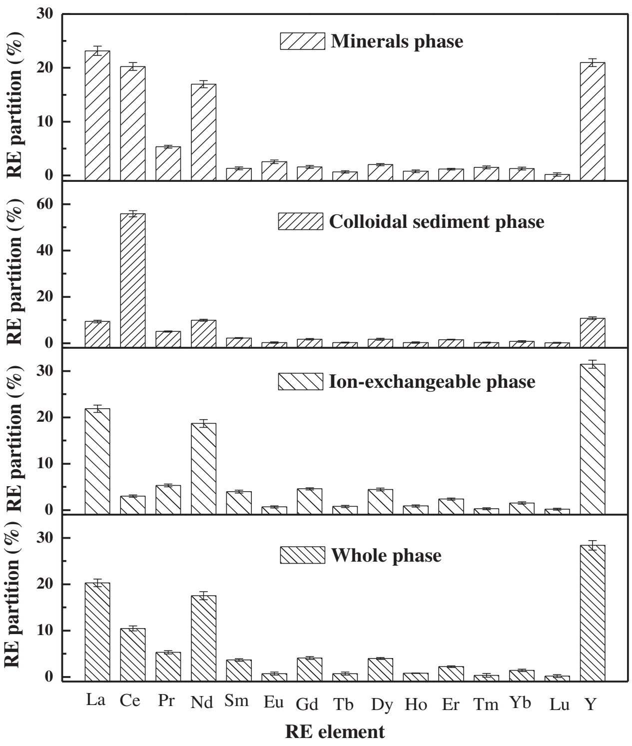

Fig. 2. Rare earth partition in different phases for LT ore sample.

2.2. Apparatus and experimental procedure

All chemicals used in the experiments, such as $FeSO_4$, $MgSO_4$ and ascorbic acid, were of analytical grade. Unless specific stated, all the solutions were prepared with deionized distilled water and the experiments were performed at ambient temperature (ca. 25 °C).

In the column leaching process, columns of 40 mm inner diameter were used as the leaching equipment, similar to that described with other chromatographic experiments. Precision pumps (Baoding Longer Precision Pump Co., Ltd., BT100-1F) were used to control the flow rate of leaching agent to 0.60 mL/min. 300 g dried rare earth ore in a specific particle size, obtained by the method of quadrate, was packed into the column and slightly tapped to make sure that the packed bed height was of 20 cm in different experiments. The ore in the column was eluted with leaching agent in a certain pH. Leaching liquor was collected from the bottom of column, and every 25 mL leaching liquor was collected as one sample. Finally, there were a total of 10 samples and 250 mL leaching liquor in the experiments. The existing state of rare earth in the leaching residues was also determined with the sequential fractionating extraction methods (Chi et al., 2005).

The concentration of rare earth elements, aluminum and iron in the leaching liquor samples were analyzed by ICP-AES (PerkinElmer, Co., Ltd. Optima 8300). The pH of leaching liquor samples was tested by pH meter (Mettler Toledo, Co., Ltd. M400). From the analysis results, the rare earth leaching efficiency (η, %) and Ce partition (δ, %) in total 250 mL leaching liquor are calculated according to the following Eqs. (2) and (3):

$$\eta = \varepsilon_v/\varepsilon_0 \qquad \text{Eq. (2)}$$