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Leaching of rare earths from mechanochemically decomposed bastnaesite

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ABSTRACT

The leaching process of rare earths from mechanochemically decomposed bastnaesite was investigated. The effects of temperature, HCl concentration and liquid-solid ratio on leaching kinetics were studied. The results show that the leaching efficiency of rare earths quickly reaches 90.7% after 10 min (50 °C; 2.5 mol/L HCl; liquid-solid ratio 10:1). The changes of specific surface area, pore volume and morphology during mechanochemical decomposition and leaching processes were examined by SEM and BET analyzer. To give a better description for the leaching kinetics, the models considered the variations of H^+ concentration with leaching, particle shape and residual amount, indicating that the leaching process was controlled by chemical reaction. The mechanochemical processing loosened the surface structure as well as increased effective reaction area, so improving leaching rate and enhancing leaching process.

1. Introduction

Bastnaesite ($REFCO_3$) is an important light rare earth resource, and provides toward 70% rare earth production in the world (Cen et al., 2018; Huang et al., 2014, 2016a, 2016b). The NaOH decomposition method is a typical decomposition method, and it decomposes directly bastnaesite into RE $(OH)_3$, followed by HCl leaching to extract rare earths. However, it is difficult to directly digest the dense mineral surface using concentrated alkaline, so the method faces low recovery of rare earths, high alkali consumption and a large amount of alkaline waste water (Wang et al., 2017).

Nowadays, mechanical milling is widely employed in hydrometallurgy and is used for the chemical reactions and physicochemical changes (Balaz and Achimovicova, 2006; Srikanth et al., 2016). The changes have great positive effects on the processes containing the activated minerals (Romeis et al., 2016). Mechanochemical treatment for minerals mainly involves two means: one is that minerals are preferentially milled then participate in chemical reactions (Balac, 2000; Palaniandy, 2015); another is that mechanical milling and chemical reactions are combined into one step (Abdel-Rehim, 2005; Zhang and Zhao, 2009; Zhao et al., 2011). In previous studies, we employed the combination of mechanical milling and caustic soda decomposition of bastnaesite, and obtained the good results: 92% of decomposition efficiency was achieved under such conditions: 180 °C, NaOH concentration 56%, liquid-solid 0.8:1 and 60 min (Liu et al., 2019). After that, the product RE $(OH)_3$ is leached by HCl to extract rare earths, so the impact of the mechanochemical treatment on downstream leaching process should be further studied.

A lot of studies have reported the influence of mechanochemical treatment involving mechanical activation and mechanochemical activation on subsequent leaching process. Akhgar and Pourghahramani (2015) studied impact of mechanical activation and mechanochemical activation on natural pyrite dissolution. The results showed that mechanochemical activation was more able to enhance the leaching of pyrite than mechanical activation. Liu et al. (2019) studied the mechanochemical decomposition of the mixed rare earth concentrate in the NaOH-CaO-H_2O system, followed by HCl leaching to extract rare earths. Comparing to the pressurized decomposition (without grinding), mechanochemical treatment improved leaching efficiency of rare earths from 58.9% to 91.8%. Such an improvement was attributed to a loosened surface structure and increased reactive area. Tang et al. (2010) studied changes of Al extraction with time using unactivated and activated kaolin residues. The results suggested that Al extraction efficiency presented a approximately linear increase towards 45° with time as leaching unactivated residue. After the residue was activated, Al extraction efficiency more quickly increased with time, similar to a logarithmic increase. This clearly demonstrated that mechanical activation could accelerate leaching process and improve leaching rate. Then effect of mechanical activation on the leaching kinetics was investigated. The kinetics of copper leaching from copper sulfide through

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mechanical activation was performed by Lee et al. (2018), and the results indicated that mechanical activation produced an increase in leachability and a decrease in activation energy and that the leaching process was controlled by chemical reaction. Consequently, it can be inferred that mechanochemical activation of bastnaesite, herein called as mechanochemical decomposition (Liu et al., 2019), would have a positive effect on the next operation of leaching rare earths.

This paper aims to study the leaching of rare earths from mechanochemically decomposed bastnaesite. Previous works have clearly confirmed the fact that mechanochemical processing can strengthen the next operation of leaching. Generally, the mechanochemical effect is investigated by the physicochemical changes in original minerals. The paper is from a new perspective, by studying the physicochemical changes and the kinetics in the leaching process, in return to find the mechanochemical strengthening mechanism. Thus, the effects of several factors, such as temperature, HCl concentration and liquid-solid ratio on the leaching of rare earths were investigated. Also, the physicochemical changes and kinetics during the leaching were determined.

2. Experimental

2.1. Materials

The bastnaesite used in the experiments was from Mianning, Sichuan. The main chemical composition and phase composition are shown in Table 1 and Fig. 1, respectively. The cumulative mass fractions do not sum up to 100% in the table because of the unaccounted composition the carbonate. NaOH used in the experiments was analytical grade reagent from Tianjin Chemical Reagent No. 3 Factory; all the solutions were prepared with distilled water.

2.2. Mechanochemical decomposition

Ball milling and alkaline decomposition of bastnaesite were carried out in a common step using in the 250 mL ball-mill autoclave with a stainless steel interior. The experiments were performed with a rotational speed of 60 r/min at 180 °C for 60 min. The 132 stainless steel balls with three different dimensions φ8 mm, φ10 mm and φ12 mm at the same ratio were added. For NaOH solution used in the experiments, its concentration and liquid to solid ratio were kept constant at 56% and 0.8:1, respectively. After the mechanochemical decomposition was over, the slurry gained was discharged into a beaker and was washed using distilled water at 70 °C for 20 min to remove fluorine. The mass ratio of the fluorine removed and total fluorine in bastnaesite was calculated as decomposition efficiency of bastnaesite. The residue after washing was dried at 60 °C and then used in subsequent leaching experiments.

2.3. Leaching

Leaching experiments were performed in a 250 mL three-neck flask glass placed in a thermostat. Agitation was provided by a mechanical agitator. A certain amount of HCl solution (2.0 mol/L–3.0 mol/L; 50 mL–75 mL) was added into the flask glass and heated up to the set temperature (30 °C–90 °C). When the temperature stabilized, the experiments started with addition of 5 g decomposition residue after washing under a rotational speed of 300 rpm. At selected time intervals, 1 mL of slurry was withdrawn and filtered. The leaching liquor was used to analyze the content of rare earths. The content of rare earths in the leaching liquor was analyzed by inductively coupled plasma spectrometer (ICP, Prodigy XP). The leaching efficiency of rare earths was calculated by Eq. (1).

$$\eta = \frac{c \times v \times M}{w \times m} \quad (1)$$

where η is the leaching efficiency of rare earths, %; c is the concentration of rare earths in the leaching solution, mol/L; v is the volume of the leaching liquor, L; M is the relative atomic mass of rare earths, g/mol; m is the mass of basnaesite, g; w is the mass percent of rare earths in basnaesite, %.

Table 1
Chemical composition of bastnaesite.

Compositions	RE_2O_3	F	Fe	SiO_2	CaO
Wt%	77.66	8.01	0.81	0.41	0.14

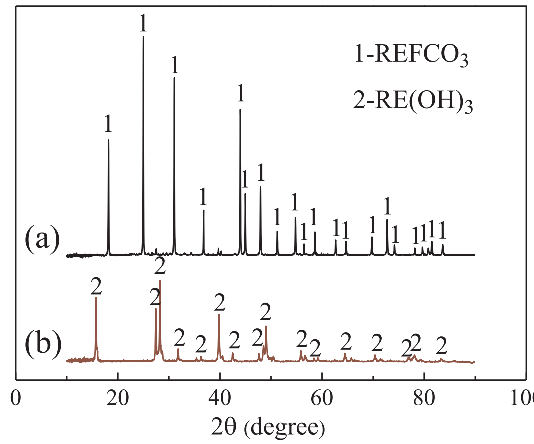

Fig. 1. The XRD patterns of bastnaesite (a) before and (b) after mechanochemical decomposition.

2.4. Experimental analysis

The rare earth content was analyzed by inductively coupled plasma (ICP, Prodigy XP) spectrometer. The BET specific surface area was obtained using surface area and porosity analyzer (ASAP2020, Micromeritics). The microstructure of the samples was collected by scanning electron microscopy (SEM, SU8010) and energy dispersive spectrometer (EDS, XFlash SVE III). The phase composition was identified by the X-ray diffractometer (XRD, PW3040/60).

3. Results and discussion

The phase compositions of bastnaesite and decomposition residue are shown in Fig. 1. The results showed that $REFCO_3$ was the main phase in bastnaesite. After mechanochemical decomposition, reflection peaks of $REFCO_3$ disappeared but RE $(OH)_3$ became the main phase in the residue. This indicated that bastnaesite was decomposed and transformed into rare earth hydroxide. The rare earth hydroxide was easy to be leached by HCl.

3.1. Effect of temperature

Fig. 2 shows the changes of rare earth leaching efficiency with temperatures ranging from 30 to 90 °C as function of time. Increased temperatures facilitated rare earth leaching. The leaching efficiency obviously increased with increasing temperature from 30 °C to 50 °C. Above 50 °C, the leaching efficiency of rare earths presented similar results after 10 min, but it could reach more quickly leaching equilibrium with raising temperature. The leaching equilibrium was achieved after 5 min when temperature is above 70 °C while the equilibrium was obtained after 10 min at 50 °C. The leaching efficiency of rare earths reached 90.7% after 10 min at 50 °C.

For the leaching of RE $(OH)_3$ without milling, the authors concluded that leaching equilibrium was reached at 70 °C for 30 min (Dou et al.,