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Influence of microwave heating on the extractions of fluorine and Rare Earth elements from mixed rare earth concentrate

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ABSTRACT

A novel process was proposed to treat the mixed rare earth concentrate by utilizing the microwave radiation. The influences of microwave heating on the mechanism of decomposition, microstructure of mixed rare earth concentrate, the behavior of fluorine leaching by water and the rare earth elements(REEs) leaching by hydrochloric acid were investigated. The results showed that bastnaesite and monazite were decomposed efficiently to rare earth oxide, and fluorine containing compounds were converted to fluoride after the microwave treatment. However, the bastnaesite and monazite were partly decomposed to REEs hydrate after treating with the conventional heating (convective heating). The recoveries of fluoride in the solutions of water and REEs in the solution of hydrochloric acid by leaching the concentrate treated with microwave radiation reached 67.1% and 82.5%, which were much higher than for those with conventional heating process (38.5% and 47.4% respectively). The increase in the recovery of fluorine and REEs is attributed to the phase transformation of REEs minerals due to the microwave characteristics of the rapid internal heating and energy transfer.

1. Introduction

The mixed rare earth concentrate (shortened as mixed concentrate in the following text) is an important resource of light rare earth to extract REEs (Wu et al., 2004), which is composed of bastnaesite and monazite (Li et al., 2013a; Bian et al., 2007), and the mass ratio of bastnaesite($REFCO_3$) to monazite($REPO_4$) is in a range from 1:1 to 9:1 (Wu et al., 2010). At present, the mixed concentrate is generally treated by the method of sulfuric acid decomposition, which is a simple and efficient method for the process of the low grade ore (Zhu et al., 2003). However, one of the major factors, which limit the development of sulfuric acid decomposition, is the off-gas of sulfur dioxide and hydrogen fluoride. Due to the difficulty of recycling the SO_2 and HF, the process causes a serious environmental pollution (Sun et al., 2007). In order to avoid the pollution from SO_2 and HF, the method of roasting decomposition with sodium hydroxide solution is utilized. In the roasting decomposition process, the solution of sodium hydroxide (60%–70%) is required with the liquid/solid ratio of 1.2 mL/g, so the consumption of sodium hydroxide is very high up to 1.8 t per ton of the mixed concentrate. Meanwhile, a large amount of waste water is produced for removing the NaF and Na_3PO_4 as by-products and NaOH as excessive reactants after roasting decomposition (Wu et al., 2006). 60 m^3 waste water, at least, will be produced during processing one ton of mixed concentrate (Xu, 1995). And it is difficult to recycle the fluoride from the waste water. The problems of waste water and the amount of consumption of sodium hydroxide have been identified as the key limitations of the roasting decomposition method with sodium hydroxide solution. Thus, it is necessary to develop new techniques for processing mixed concentrate, to alleviate burdens of economy and environment.

The applications of microwave in mineral processing were investigated over the past three decades and have been of particular interest in mineral processing and extractive metallurgy (Al-Harahsheh et al., 2005). As microwave radiations heat the material at the molecular or atomic level and only affect the polar substances, microwave heating is a selective heating process. While the conventional heating is a process of convective heating by gas or liquid, microwave heating is more rapid heating process compared with the conventional heating (Huang and Rowson, 2002; Omran et al., 2014). Nanthakumar et al. (2007) studied the difference of microwave heating and conventional heating for a gold ore. It was found that both the total carbon removal rate and the heating rate were higher with a lower the specific energy consumptions for microwave heating than that for the conventional heating. Because of the different microwave absorption characteristics, trans-granular and inter-granular fractures can be induced among the different minerals or the minerals matrices (Haque, 1999; Chang et al., 2008; Schmuhl et al., 2011). Olubambi et al. (2007) studied the influence of microwave heating on the processing and dissolution behavior of low-grade complex sulphide ores. It was found that Pyrite exhibited an absorbing characteristic absorbing microwave energy and transforming it into heat, and then causing differential expansion which induces fractures within the pyrite matrices. The influence of microwave pre-treatment of a low grade copper ore (Schmuhl et al., 2011)

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showed that the copper recovery was enhanced as a result of an increase in the porosity of the ore particles after microwave pretreatment. Li et al. (2013b) studied the decomposition of rare earth concentrate with sulfuric acid by microwave-assisted heating. It was stated that the bastnaesite and monazite as polar substances can be heated by microwave radiation, while the gangue (silica, fluorite) cannot be heated. Due to the microwave's amazing capability of accelerating chemical reactions (Huang and Rowson, 2002; Hwang et al., 2002), it is possible to decompose the mixed concentrate under a lower temperature and lower consumption of alkali for the microwave heating than that for the existing process.

The aim of this research is to establish the phase transformations of REEs and fluoride in the process of microwave heating of mixed concentrate and compare the phase transformations after a microwave heating and a conventional heating. Further, the influence of microwave heating on the leaching of fluoride and REEs was investigated.

2. Experimental

2.1. Sample materials and their characterization

The mixed concentrate worked in this experiment was from the Baotou in China and was dried at 90 °C for 24 h to remove the free moisture water. The particle size of the mixed concentrate was below 74.0 μm and the color was gray. The chemical compositions of sample were analyzed and listed in Table 1. The analytical grade reagents were used in the experiment, including hydrochloric acid from Beijing Chemical Works and sodium hydroxide (NaOH) from Tianjin Chemical Reagent No. 3 Factory. And all aqueous solutions were prepared with distilled water.

2.2. Experimental process and analysis

The microwave equipment worked in this experiment was from the key laboratory of unconventional Metallurgy, Ministry of Education, Kunming University of Science and Technology, China. Experiments of roasting decomposition of mixed concentrate with microwave heating were carried out at the power level of 1000 W with a frequency of 2.45 GHz. The mixed concentrate was mixed with sodium hydroxide particles by mixed grinding, and the mass ratio of sodium hydroxide to mixed concentrate is 35.4%. This is a theoretical value to decompose the bastnaesite and monazite followed the reaction Eqs. (1)–(2). The sample, which was placed in a ceramic crucible with an 80.0 mm diameter, was put in the center of microwave chamber. Due to the limited size of the crucible, only 50.0 g sample was treated for each experiment. The temperature set to 140 °C was reached in 5 min. The thermocouple was inserted into the center of the sample in the microwave heating process and into the center of the furnace in the conventional heating process, so the measured temperature can more closely reflect the sample temperature than that in the conventional heating process which considered the furnace temperature as the sample temperature. On completion, the ceramic crucible was removed out and was cooled in air. Then, the sample was used to leach fluoride by water. The solution was rapidly separated by vacuum filtration, and the leaching liquid was used to analyze the content of fluoride by Lanthanum-Alizarin Complex one Spectrophotometry (Fu, 2004). The filter residue after dried at 60 °C was used to extract REEs in the solution of hydrochloric acid(3.0 mol/L) with the 20 mL/g liquid-solid ratio. The acid leaching experiments were performed in a 500 mL glass beaker, with mechanical stirring, and in a water bath. After a certain period, the leaching solution was separated by vacuum filtration. The contents of REEs in the acid leaching liquid were analyzed by Prodigy XP ICP-OES of Teledyne Leeman, USA. The wavelengths used in ICP measurements are 413.765 nm for Ce, 333.749 nm for La and 386.333 nm for Nd.

The content analysis of Ce^{4+} in the microwave heating sample was determined by Ferrous Ammonium Sulfate Titration (Fu, 2004). The result was measured for three times to obtain the average values. Relative standard deviation was found to be within ±0.5%. The phase composition was determined by the PW3040/60 diffraction instrument with CuK_α radiation. The microscopic morphology was observed by a scanning electron microscope (SEM. SU-8000, Japan). The BET specific surface area was obtained with a specific surface area and bore diameter tester (ASAP2020M).

Table 1
Chemical composition of mixed concentrate (mass fraction, %).

RE_xO_y	Ce	La	Nd	F	P	Ca
48.94	23.2	11.1	6.94	9.18	3.14	8.90

3. Results and discussion

The microscopic morphology and X-ray diffraction pattern of mixed concentrate were analyzed, and the results were showed respectively in Figs. 1 and 2. It is seen that the irregular spherical particles presented a random and smooth surface (see Fig. 1(a)). From the XRD patterns (Fig. 2), it can be seen that the mixed concentrate was mainly composed of $REFCO_3$, $REPO_4$ and CaF_2. The proportions of $REFCO_3$ and $REPO_4$ in the mixed concentrate can be measured according to the content analysis of Ce^{4+} after roasting the mixed concentrate at 1000 °C (Wu, 2005; Li et al., 2013a). The results revealed that the mass percentages of $REFCO_3$ and $REPO_4$ in mixed concentrate were 43.0% and 22.7%, respectively. Then, according to the contents of REFCO3 and fluorine showed in Table 1 the ratios of fluorine($REFCO_3$)/total fluorine and fluorine(CaF_2)/total fluorine can be measured, which were 41.2% and 58.8%, respectively.

3.1. Phase transformation in the microwave heating process

3.1.1. Influence of heating time on the phase transformation

In order to study the decomposed behavior of mixed concentrate in the microwave heating process, 50.0 g mixed concentrate and 17.7 g NaOH particles were treated by microwave radiation for different times. From the XRD patterns of Fig. 3, it can be seen that the samples had the same obvious diffraction peaks of rare earth oxide at the two theta (2θ) of 28.44°, 32.72°, 47.09°and 55.90°, sodium fluoride at the 2θ of 39.09°and 55.78°. And the heating time had no influence on the phase transition, that is, all the XRD patterns with different heating times (from 10 to 40 min) were similar (Fig. 3). However, compared with the XRD pattern of mixed concentrate as shown in Fig. 2, the diffraction peaks of $REFCO_3$ and $REPO_4$ disappeared (see Fig. 3).

The mixed concentrate employed in the experiment mainly consists of three rare earth elements (Ce, La and Nd), presenting in the form of rare earth oxide after microwave heating process. What's more, the trivalent cerium in the mixed concentrate was oxidized to tetravalent cerium in the form of CeO_2 due to the microwave heating process was conducted in air and the ratio of content of Ce^{4+} and total content of cerium element was 78.3%. And then the CeO_2 combined with Nd_2O_3 generated complex oxide ($Ce_{0.5}Nd_{0.5}O_{1.75}$) (Sun et al., 2001). With the decomposition of $REFCO_3$, fluoride was converted to sodium fluoride. Part of CaF_2 was also converted to sodium fluoride, which was confirmed in the experiment of leaching fluoride. Thus, compared with XRD pattern of mixed concentrate (Fig. 2), we concluded the phase transformation process to be occurred in microwave heating process as follows:

$$2REFCO_3 + 6NaOH = RE_2O_3 + 2NaF + 2Na_2CO_3 + 3H_2O \quad (1)$$

$$2REPO_4 + 6NaOH = RE_2O_3 + 2Na_3PO_4 + 3H_2O \quad (2)$$

$$2Ce_2O_3 + O_2 = 4CeO_2 \quad (3)$$