Thermal decomposition and oxidation of bastnaesite concentrate in inert and oxidative atmosphere☆

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ABSTRACT

To clearly elucidate the oxidative roasting behaviors of the bastnaesite, the thermal decomposition and oxidation of the bastnaesite concentrate in inert and oxidative atmosphere have been investigated in detail. Experimental data indicated that the initial decomposition temperature of the concentrate under N_2 atmosphere is 150 °C higher than that under O_2 atmosphere, most likely because the oxidation of the cerium induces the decomposition of the concentrate. For the roasted samples under N_2 atmosphere at 500 °C and above, the oxidation efficiency of the cerium is 19.8%–26.8% because of the fact that rare-earth fluorocarbonate is first decomposed to form rare-earth oxyfluoride and CO_2, and the cerium oxyfluoride is then partially oxidized by the CO_2 gas. The rest cerium in these samples can be further oxidized in air at room temperature, with the oxidation efficiency of the cerium gradually increasing to above 80% in 7 d. This can be attributed to the obvious changes in the inner morphology of the roasted samples under N_2 atmosphere at high temperatures, which largely induce the diffusion of the air and improves the oxidation activity of CeOF, and further induces the oxidation of CeOF by the air. XRD and XPS techniques were used to further verify the significant differences in the thermal decomposition behaviors of the bastnaesite concentrate under N_2 and O_2 atmosphere. Moreover, no oxidation of Pr^{3+} to Pr^{4+} in the roasted samples under both N_2 and O_2 atmosphere is observed. This gives an overall understanding of the oxidative roasting of the bastnaesite concentrate without additives.

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1. Introduction

Rare-earth elements (REEs) have wide application in permanent magnets, optics and lasers, catalysts, ceramics, and energy conversion.[1–5] China has been widely recognized as a country with abundant rare earth resources, and provides over 85% of the world's total REEs output.[6,7] In China, bastnaesite is mainly deposited in Inner Mongolia, Sichuan, and Shandong Province, and gravity-magnetic separation or flotation has usually been employed to produce a bastnaesite concentrate. Typical bastnaesite concentrate contains 8 wt%–10 wt% fluorine and 0.2 wt%–0.3 wt% thorium in addition to REEs, of which about 50 wt% is ceria oxide (CeO_2).[8–11]

Generally in industrial production, oxidative roasting-hydrochloric acid leaching has been widely used for treatment of the bastnaesite concentrate.[11,12] The concentrate is first roasted at 500–700 °C, with subsequent hydrochloric acid leaching to form a non-cerium rare-earth chloride solution and a cerium concentrate containing 65 wt%–70 wt% REO and 55 wt%–60 wt% CeO_2. The cerium concentrate is digested with caustic soda to convert the rare-earth fluorides to hydroxides, which are then dissolved in hydrochloric acid to form a rare-earth chloride solution. The rare-earth chloride solutions are finally used as raw materials for solvent extraction after impurities removal. This process is disadvantaged by the very complicated processes, the relatively low rare earth recovery, and the disposal of large amounts of sodium fluoride wastewater, leading to serious resources depletion and environmental degradation.[12,13]

To solve the problems of fluorine-bearing wastewater and low recovery of rare earths in the conventional process, thermal decomposition of the bastnaesite concentrate using sodium carbonate,[14,15] calcium oxide,[16,17] rare-earth nitrate,[18] and even

mechanical activation[19] have been developed in recent decades, but have not been successfully put into industrial practice yet. To reduce reliance on auxiliaries, avoid unnecessary steps and minimise hazards, which are the three of the "Twelve Principles of Green Chemistry",[20] as well as considering the potential in successful industrial practice, oxidative roasting without additives seems to be a greener route for the treatment of the bastnaesite concentrate, and it is also indispensable to develop a cleaner technology based on existing roasting-leaching process. Therefore, an overall understanding of the oxidative roasting of the bastnaesite concentrate without additives is of vital importance. Existing researches on the thermal decomposition of the bastnaesite concentrate without additives have focused on the phase transition using X-ray diffraction (XRD) and thermogravimetric-differential thermal analysis (TG-DTA),[21–24] but the behaviors of the REEs with electrovalence changes like Ce and Pr in inert and oxidative atmosphere have not been systematically investigated yet, which provides the impetus for this work.

In this work, to clearly elucidate the thermal decomposition of the bastnaesite concentrate, the decomposition behaviors in inert and oxidative atmosphere have been investigated in detail. The oxidation behaviors and phase transformation of the REEs with electrovalence changes in the bastnaesite concentrate under N_2 and O_2 atmosphere have been intensely studied, as well as the fluorine loss.

2. Experimental

2.1. Materials

The bastnaesite concentrate used in this work was obtained from the Dechang mining area, southwestern Sichuan Province, China. The chemical composition and partitioning of rare earths of the bastnaesite concentrate are listed in Tables 1 and 2, respectively. The mineralogical analysis of the bastnaesite concentrate is presented in Fig. 1. It can be seen from Fig. 1 that the bastnaesite concentrate mainly consists of rare-earth fluorocarbonate ($REFCO_3$) and calcium fluoride (CaF_2). High-purity nitrogen with N_2 mass fraction of 99.999% and industrial oxygen with O_2 mass fraction of >99.2% were used in this work. Other reagents used were all of analytical grade.

2.2. Experimental procedure

Roasting experiments were conducted in a quartz horizontal tubular furnace, where the roasting temperature and the roasting time could be controlled. The quartz tube was first flushed with high-purity nitrogen or industrial oxygen at a constant gas flow rate (0.6 L/min), and then heated to a preset temperature at a heating rate of 10 °C/min. After reaching the preset temperature, 50 g of the bastnaesite concentrate (dried at 105 °C for 3 h before use) was taken in an alumina boat and placed at the center of the quartz tube that was inserted in the tubular furnace, and then held at the preset temperature for 2 h. After that, the quartz tube was rapidly taken out of the tubular furnace and then rapidly quenched with water to room temperature. The roasted sample was then stored with seal at room temperature before the pretreatment for analysis.

2.3. Analysis

2.3.1. Determination of weight loss of the bastnaesite concentrate

The mass losses (W_L) at different temperatures were determined by weighing the bastnaesite concentrate and the roasted sample, which can be expressed as Eq. (1).

$$W_L = \frac{w_0 - w}{w_0} \times 100\% \tag{1}$$

where w_0 and w refer to the mass of the bastnaesite concentrate and the roasted sample, respectively.

2.3.2. Determination of CeO_2 mass fraction

Determination of the mass fraction of total CeO_2 (C_{tot}): 0.5–1.0 g (accurate to 0.0001 g) of the solid sample, 30 mL concentrated phosphoric acid (H_3PO_4) and 2 mL perchloric acid ($HClO_4$) were first added into a beaker flask, and then slowly heated until the sample was completely dissolved.[25] 20 mL dilute sulfuric acid (H_2SO_4) was added to the beaker flask, which was then rapidly quenched by water.

Determination of the mass fraction of $Ce^{(IV)}O_2$ ($C_{Ce(IV)}$): 0.5–1.0 g (accurate to 0.0001 g) of the solid sample and 30 mL concentrated H_3PO_4 was first added into a beaker flask, and then slowly heated under the protection of high-purity nitrogen until the sample was completely dissolved.[25] 20 mL dilute H_2SO_4 was added to the beaker flask, which was then rapidly quenched by water.

The mass fraction of total CeO_2 of the sample (C_{tot}) and total $Ce^{(IV)}O_2$ of the sample ($C_{Ce(IV)}$) were then rapidly determined by the redox titration using $(NH_4)_2Fe(SO_4)_2$. At least triplicate analyses were carried out for each sample.

Thus, the oxidation efficiency of cerium (η_{ox}) can be expressed as Eq. (2).

$$\eta_{ox} = \frac{w \times C_{Ce(IV)} - w_0 \times C^0_{Ce(IV)}}{w_0 \times \left(C^0_{tot} - C^0_{Ce(IV)} \right)} \times 100\% \tag{2}$$

where C^0_{tot} and $C^0_{Ce(IV)}$ refer to the mass fraction of total CeO_2 and $Ce^{(IV)}O_2$ in the bastnaesite concentrate, respectively, $C_{Ce(IV)}$ refers to the mass fraction of $Ce^{(IV)}O_2$ in the roasted sample.

2.3.3. Fluorine determination with fluoride ion-selective electrode

0.1–0.2 g (accurate to 0.0001 g) of the solid sample was first digested with 4 g of sodium hydroxide (NaOH) in a nickel crucible at 600 °C for 40 min, and the digested product was then leached with 100 mL deionized water (H_2O) and dilute hydrochloric acid (HCl) at room temperature for 1 h before it was filtrated. Dilute HCl and sodium acetate (CH_3COONa) were finally used to adjust the pH value of the obtain filtrate to 5.0–6.0. Fluorine determination was conducted using a fluoride ion-selective electrode.[26] The fluoride ion-selective electrode (PF-1-01) was used in combination with a single-junction saturated calomel reference electrode (232-01),

Table 1
Chemical composition of the bastnaesite concentrate (wt%).

REO	CaO	SrO	MgO	Fe_2O_3	Al_2O_3	TiO_2	MnO	ThO_2	F	CO_2
65.74	3.33	3.27	0.05	0.82	0.10	0.16	0.05	0.13	7.98	17.98

Table 2
Partitioning of rare earths of the bastnaesite concentrate (wt%).

La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3
39.93	45.98	3.83	8.95	1.17	0.10	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.00