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Flotation-magnetic separation for the beneficiation of rare earth ores



^a College of Resources and Civil Engineering, Northeastern University, Shenyang, Liaoning, PR China

^b Institute of Multipurpose Utilization of Mineral Resources, Chinese Academy of Geological Science, Chengdu, Sichuan, PR China

Wenliang Xiong^{a,b}, Jie Deng^{b,*}, Binyan Chen^b, Shanzhi Deng^b, Dezhou Wei^a

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ABSTRACT

As rare earth metal prices fall, the low-cost beneficiation of their minerals has become essential. Flotationmagnetic (FM) separation is a newly-developed technology for the economic recovery of rare earth elements from the Dalucao ore. The FM process selectively agglomerates the rare earth particles while separating them from gangue minerals by bubble flotation. The agglomeration of fine bastnaesite particles has been observed by optical microscope and SEM combined with EDS which approves that the collector is selective for the fine mineral of bastnaesite. The quality of the flotation products are further improved by magnetic separation. The FM process has been successfully applied in the industrial production of the Dalucao rare earth ore located in Sichuan, China. The average rare earth oxide (REO) grade of the obtained rare earth concentrate was 65% in the latest 12-month production run with an average recovery of 55%.

1. Introduction

Rare earth elements (REEs) include the fifteen lanthanide elements along with two chemically similar elements yttrium and scandium. These elements are split into two subgroups, with La to Sm classified as light rare earth elements (LREEs) and the remaining including yttrium classified as heavy rare earth elements (HREEs) (Kumari et al., 2015). In recent years, the demands for rare earth elements has surged in part due to their increased use in diverse industrial applications, including high-strength magnets, phosphors, polishing compounds, catalysts, and clean energy technologies (Golev et al., 2014).

More than 250 REE-bearing minerals have been discovered, but most have very low REE concentrations in the range 10–300 ppm (Adam et al., 2013). The most commonly mined rare earth minerals are bastnaesite, monazite, xenotime, and various ion-adsorption REEs (Chelgani et al., 2015; Kanazawa and Kamitani, 2006). Before the 1960s, most rare earth resources were extracted from monazite in beach placers, but with the exploitation of Mountain Pass in the United States and the Bayan Obo mine in China, bastnaesite became the chief source of the rare earth minerals (Klinger, 2015). They are commonly separated from gangue by froth flotation, gravity concentration, magnetic separation, or combinations thereof based on their specific physical characteristics (Zhou et al., 2014; Adam et al., 2014; Yang et al., 2015; Xia et al., 2015a, 2015b).

Within the Sichuan province lies the second largest rare earth deposit in China containing bastnaesite ($CeCO_3F$) as the primary mineral (Wübbeke, 2013; Liu et al., 2015). Before 2000, gravity separation

* Corresponding author. E-mail address: dengjie23@126.com (J. Deng).

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performed with a shaking table was the only beneficiation process capable of recovering the rare earth minerals. This primitive process resulted in huge losses of their resources and heavy pollution of the mine environments. Between 2000 and 2010, magnetic separation and flotation were introduced to beneficiate the Sichuan rare earth ore. A combined "gravity-magnetic-flotation" process was developed (Li et al., 2002; Xiong and Chen, 2009), leading to significant increases in rare earth oxide (REO) content and recovery from the Maoniuping rare earth concentrate. However, REO recovery from Dalucao rare earth ores remained low at about 20%.

Dalucao rare earth ore is located in the southern part of the Mianning-Dechang REE Belt in the western Sichuan province (Liu et al., 2015). Like most rare earth deposits, the Dalucao deposit is mined from an open pit. The traditional beneficiation processes used including the combined gravity-magnetic-flotation process, dry magnetic separation, and heated flotation have been applied in the plant, resulting in terrible working conditions, elevated production costs, and a lowered beneficiation index, with a 50% average REO content in concentrate and 20% recovery.

In this study, the use of FM separation was investigated in order to improve the grade of the REO recovered from the Dalucao rare earth ore. The main factors affecting the FM process were tested, and improvements of the FM process are discussed here.

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Table 1

Chemical composition analysis of raw material from the Dalucao deposit (%).

Element	TREO	SiO_2	CaF_2	BaO	Fe_2O_3	Al_2O_3	MgO	CaO	S
Content Element	2.40 K ₂ O	28.59 MnO	14.98 C	3.99 Pb	3.07 SrO	9.31 ThO ₂	1.20 Zn	16.40 Ti	1.92 Nd
Content	4.48	0.23	1.21	0.20	8.36	0.0073	0.023	0.31	0.19

2. Material and methods

2.1. Raw materials

The raw material used in this work originated from the Dalucao deposit located in the Sichuan province in China. A 1000-kg representative ore sample was collected and sent to the lab. The sample was initially crushed into 3-mm particles using a combination of jaw crushing, sieving, and roll crushing, and then blended and divided to support our mineralogical and beneficiation studies. Inductively-Coupled Plasma-Optical Emission Spectrometry (ICP-OES) was used to determine the elemental content in the sample. The results of this complete chemical analysis of the representative sample are given in Table 1, while that of the assemblage of rare earth elements is shown in Table 2.

A mineral liberation analyzer (MLA) was used to determine the mineral composition of the raw ore, with its results shown in Table 3. The primary rare earth mineral in the Dalucao deposit was bastnaesite, with 2.40% REO, and the sample also contained a significant amounts of fluorite and Sr/Ba sulfide, which have similar floatabilities to bastnaesite. Ce, La, Pr, Nd, and Sm were the other primary rare earth elements, suggesting that the REO were dominated by LREE. Calcite and quartz were the dominant gangue minerals.

The particle size distribution is shown in Fig. 1, and the liberation of bastnaesite is listed in Table 4. Bastnaesite was finely disseminated with close intergrowth with barite, celestite, and fluorite.

2.2. Reagents

Ethyl thiocarbamate was used as the collector during the flotation of the sulfide minerals. Sodium silicate with a modulus of 2.8 was used as the depressant, and the rare earth collectors used, H205 and LF, were obtained from the Baotou Steel Rare Earth Group High-Tech Co. Ltd. Both Wx and Wx-1 were self-developed rare earth collectors with different components. EM-312 was used as a frother to improve the speed of rare earth flotation and reduce the flotation temperature to 8–10 °C.

2.3. Bulk flotation

The head sample was blended and split into 300-g feed charges for the respective tests, which were then milled at a solid-liquid ratio of 60% using a laboratory-scale stainless steel rod mill to achieve a certain grinding fineness. The milled slurry was transferred to a 1 L XFD

Table 2

Rare earth element	assemblage of	f raw materials	from the Dalucao	deposit (%).
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Element	Content	Element	Content
Ce ₂ O ₃	1.20	Dy_2O_3	< 0.005
La_2O_3	0.77	Pr_6O_{11}	0.12
Nd ₂ O ₃	0.29	Ho ₂ O ₃	< 0.005
Y_2O_3	< 0.005	Er_2O_3	< 0.005
Sm_2O_3	0.022	Tm_2O_3	< 0.005
Eu_2O_3	0.0054	Yb ₂ O ₃	< 0.005
Gd_2O_3	< 0.005	Lu_2O_3	< 0.005
Tb ₄ O ₇	0.0055	TREO	2.40

Table 3

Mineralogical composition of raw material from the Dalucao deposit (%).

Mineral	Weight	Mineral	Weight
Bastnaesite	3.50	Galena	0.25
Monazite	0.02	Sulfide minerals of Strontium and Barium	14.50
Strontianite	7.70	Fluorite	15.00
Celestine	1.20	Limonite	2.00
Barite	2.00	Silicate and other carbonate minerals	53.83



Particle Size (mm)

Fig. 1. Particle size distribution of bastnaesite in the raw ore obtained from the Dalucao deposit.

Table 4

Liberation of bastnaesite (%).

Grinding Fineness (finer than	Liberated	Intergrowth		
0.074 mm)		With barite and celestine	With fluorite	
63.37	46.69	42.16	11.15	
74.37	57.14	35.22	7.64	
86.52	85.19	9.25	5.56	

flotation cell. The cell volume was chosen to obtain a 30% solid-liquid ratio, and the impeller speed was set to 1800 rpm. Sodium silicate, ethyl thiocarbamate, and EM-312 were added in sequence to float the sulfide minerals. The bulk fraction of the sulfide flotation was the feed for the rare earth flotation. The depressant, rare earth collector, and frother were added to the slurry to recover the rare earth minerals. The flotation concentrates and tailings were then filtered, dried, and weighed prior to analysis. The flotation products were analyzed by inductivelycoupled plasma-optical emission spectrometry (ICP-OES) to determine the TREO content of elements La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

2.4. Magnetic separation

The flotation concentrate was processed using wet high-intensity magnetic separation (WHIMS, ERIEZ L-4-20) to characterize the efficiency of the process. During the magnetic separation tests, the flotation slurry was added directly via an inlet to the magnetic machine with minimal flush water. The solid content of the slurry was about 15%, the flowrate about 100 mL/min, and the applied magnetic intensity 1.5 T.

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