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Mineralogical characteristic and beneficiation evaluation of rare earth carbonate wall rock

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Abstract: In order to rationalize the development and utilization of the wall rock discarded during rare earth mining, chemical analysis, inductively coupled plasma-atomic emission spectroscopy, X-ray diffraction analysis, artificial panning, optical microscope analysis, mineral liberation analysis and energy-dispersive spectroscopy were used to study the process mineralogy of the wall rock. The results show that the main useful elements in the rare earth wall rock were iron, light rare earth elements, fluorine and niobium. Iron was mainly occurrence as magnetic iron in magnetite, rare earth elements in bastnaesite and monazite, fluorine as a independent mineral in fluorite and niobium in columbite. The main useful minerals were finely disseminated, with magnetite (48.16%), bastnaesite (49.04%), monazite (42.18%), fluorite (39.30%) and columbite (63.26%) distributed in -0.030 mm particle size. The useful minerals were evaluated separately for beneficiation based on the process mineralogical characteristics of the rare earth wall rock, and the results showed that magnetite, rare earth and fluorite resources could be effectively recovered using magnetic separation, flotation, gravity concentration and leaching enrichment methods. The sequential recovery of iron, rare earth, fluorine and niobium elements produces iron concentrate (65.40% TFe at recovery of 38.03%), rare earth concentrate (50.66% REE at recovery of 62.73%), fluorite concentrate (95.23% CaF₂ at recovery of 40.34%) and niobium iron ore concentrate (1.63% Nb₂O₅ at recovery of 5.56%). This study provides recommendations for the rational development and utilization of rare earth wall rock and provides reasonable levels of recovery predictions.

Keywords: rare earth, wall rock, magnetite, fluorite, process mineralogy, beneficiation

1. Introduction

The rocks around the ore body and around the rock mass were called the wall rock. In general, the boundary between the ore body and the wall rock has been determined by systematic sampling and analysis, based on certain industrial indicators. Ore body was commonly discarded directly in tailings pond during mining, and a large amount of useful elements were wasted, especially those containing rare metals and rare earth elements.

The wall rock of rare earth deposits contains a certain amount of light rare earth elements (LREE) and heavy rare earth elements (HREE), as well as rare elements such as tantalum and niobium, and some rare earth wall rock also contains fluorite, which has a high comprehensive utilization value (Ouyang et al., 2018; Popova et al., 2014; Bai et al., 2021). In recent years, scholars worldwide have mainly focused on the comprehensive utilization research of rare earth deposits, with less research results on rare earth wall rock.

Basic enrichment methods of rare earth wall rock and rare earth deposits were similar, mainly using flotation to recover rare earth minerals, but the single flotation method was less effective, and the single

flotation method for rare earth ores with complex ore composition generally failed to achieve the quality index of rare earth products (Yu., 2001). At present, rare earth ore processing plants mainly adopt combined separation processes, which include magnetic separation-flotation, gravity separationflotation, magnetic separation- gravity separation, and combined magnetic separation- gravity separation-flotation processes (Zhang et al., 2018; Jordens et al., 2013; Balaram et al., 2019; Binnemanns et al., 2013). The combined flotation-gravity separation process of the Weishan rare earth mine in Shandong, China, successfully solved the deterioration of the middle ore caused by the single flotation method and obtained a rare earth concentration with a REE grade of 40.18% (Wang et al., 2021). Combined processes were suitable when the rare earth elements were occurrenced as independent minerals, such as bastnaesite, monazite and xenotime. When rare earth elements were adsorbed on other minerals in ionic form, the combined physical beneficiation process was less effective in enriching rare earth elements, when chemical beneficiation was suitable for enrichment (Jha et al., 2016). The use of MgSO₄ instead of (NH4)₂SO₄ as leaching agent resulted in more than 95% leaching of rare earths and reduced the leaching efficiency of aluminum (Xiao et al., 2015). However, these aforementioned enrichment methods were mainly applied to rare-earth deposits, and fewer studies were reported on the application to rare-earth ore wall rock.

In this study, the wall rock of the world's largest rare earth mine, the Bayan Obo rare earth mine in Inner Mongolia Autonomous Region, were firstly studied for detailed process mineralogical characteristics, including mineral composition and content, the occurrence state of main elements and the dissemination characteristics of main minerals. Optical microscopy analysis (ZEISS Axioskop 40, Zeiss, Oberkochen, Germany), chemical analysis, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), X-ray diffraction analysis, artificial panning, mineral liberation analysis (MLA650, FEI Company, Hillsboro, OR, USA) and energy-dispersive spectroscopy were used in the process mineralogy characterization study. Based on the mineralogical characteristics of the wall rock and extensive test results, the main useful minerals in the wall rock were evaluated for beneficiation. The purpose of this study was to provide suggestions for the rational development and utilization of rare earth wall rock and to provide a reasonable level of recovery prediction for the development and utilization of the same type of resources.

1. Materials and methods

2.1. Materials

The Rare earth carbonate wall rock from Inner Mongolia Autonomous Region, China, was used in the experiments. A representative sample of about 30 tons were selected from the waste dump for the experimental study, of which about 100 kg were used for characterization and testing.

2.2. Methods

The chemical composition of the raw ore was measured using chemical analysis and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Intrepid II XSP, Thermo Electron, Waltham, MA, USA). The mineral composition and content of the ore sample were determined by methods including optical microscopy analysis, X-ray diffraction analysis, and mineral liberation analysis (MLA).

The dissemination characteristics of the main minerals were analyzed by optical microscopy and MLA. The occurrence states of the main elements in the samples were analyzed by energy-dispersive spectroscopy (EDS). Firstly, the content of main elements in single minerals was determined by EDS, and then the mineral content results were combined. Finally, based on the results the main element balance was calculated and the element occurrence state was derived.

The study method is shown in Fig. 1. The mineral liberation analysis was conducted on MLA-650 (FEI, USA) with an acceleration voltage of 20 kV and an emission current of 129 μ A. Optical microscope analysis was performed on a ZEISS Axioskop 40 microscope. X-ray diffraction analysis was performed on a Rigaku SmartLab X-ray diffraction spectrometer employing a graphite-filtered Cu K α radiation (λ = 1.5406 Å), operated at 40 kV and 40 mA with a scanning rate of 5°/min from 2° to 70°.



Fig. 1. Research methods

1. Results and discussion

3.1. Mineralogical characteristic

3.1.1. Chemical composition and mineral composition of sample

The chemical compositions and contents of the representative initial samples are shown in Table 1. The main valued elements were iron (13.31% TFe), rare earth (2.92% REEO), niobium (0.06% Nb₂O₅), and fluorine (7.83% F). The harmful elements were sulfur (0.86% TS), phosphorus (0.48% P_2O_5), and potassium (1.84% K₂O).

Component	TFe	REEO*	Nb ₂ O ₅ *	CaF ₂	CaO	MgO	SiO_2	Al_2O_3	TS	P_2O_5
Content wt.%	13.31	2.92	0.06	7.83	18.06	8.09	17.86	5.14	0.86	0.48
Component	MnO	K ₂ O	CuO	Na ₂ O	TiO ₂	ZnO	SrO	BaO	ThO_2^*	/
Content wt.%	2.35	1.84	0.01	1.06	0.59	0.16	0.23	1.31	0.02	/

Table 1. Chemical composition of sample

*: By ICP-AES

The X-ray diffraction pattern of the sample is displayed in Fig. 2. Table 2 shows the mineral composition and content of the sample. As can be seen in Fig. 2 and Table 2, the major iron minerals in the ore were magnetite (7.73%) and hematite (2.097%). The major rare-earth minerals in the ore were bastnaesite (1.853%) and monazite (1.31%). The major niobium minerals were columbite (0.051%) and aeschynite (0.039%). The ore contained a large amount of fluorite (7.778%). The gangue minerals were mainly ankerite, biotite, orthoclase, albite, calcite, quartz and chlorite accounting for nearly 67%.

3.1.2. Main element occurrence states

The modes of occurrence of iron, fluorine, rare earth and niobium, and distribution in various minerals were shown in Fig. 3. The element iron was mainly occurrenced as magnetic iron in magnetite, and secondly occurrenced in ankerite. The element F was mainly occurrenced in fluorite, with a distribution rate of 90.39%. Rare-earth elements were mainly occurrenced in bastnaesite and monazite, and to a minor occurrenced in parisite and huanghoite. The element niobium was mainly occurrenced in columbite and aeschynite, and to a minor occurrenced in fergusonite and other minerals.

Fig. 4 shows the elemental mappings of the major rare earth and niobium minerals (Bastnaesite, Monazite, Columbite). It can be seen from Fig. 4 that the major elements in bastnaesite, monazite and columbite were well distributed and no alteration occurred within the minerals.



Fig. 2. Results of X-ray diffraction analysis

	Mineral	Formula	Content wt.%
Iron minerals	Magnetite	Fe ₃ O ₄	7.730
	Hematite	Fe ₂ O ₃	2.097
	Ilmenite	FeTiO ₃	0.280
	Limonite	FeO (OH) nH ₂ O	0.261
	Pyrite	FeS ₂	0.188
Rare-earth minerals	Bastnaesite	(Ce, La) [CO ₃]F	1.853
	Monazite	(Ce, La, Nd) PO ₄	1.310
	Huanghoite	BaCe (CO ₃) ₂ F	0.135
	Parisite	Ce_2Ca (CO_3) ₃ F_2	0.120
	Allanite	(Ce, Ca) ₂ (Fe, Al) ₃ [Si ₂ O ₇] [SiO ₄]O(OH)	0.014
Niobium minerals	Columbite	(Fe, Mn) Nb_2O_6	0.051
	Aeschynite	(Ce, Th) (Ti, Nb) ₂ O ₆	0.039
	Ilmenorutile	(Ti, Nb, Fe)O ₂	0.008
	Fergusonite	Y(Nb, Ta)O ₄	0.006
	Fersmite	$CaNb_2O_6$	0.004
	Niobium-containing		0.022
	ilmenite		0.823
Halide	Fluorite	CaF ₂	7.788
Gangue minerals	Ankerite	Ca (Mg, Fe) (CO ₃) ₂	31.861
	Biotite	K (Mg, Fe)3AlSi3O10(F, OH)2	11.008
	Orthoclase	$K_2O \cdot Al_2O_3 \cdot 6SiO_2(K[AlSi_3O_8])$	6.758
	Albite	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	6.177
	Calcite	CaCO ₃	4.332
	Quartz	SiO ₂	3.365
	Chlorite	Y ₃ [Z ₄ O ₁₀] (OH) ₂ Y ₃ (OH) ₆	3.387
	Aegirine Augite	(Na,Ca)(Fe,Mg,Al)[Si ₂ O ₆]	2.895
	Barite	BaSO ₄	1.294
	Apatite	Ca ₅ (PO ₄) ₃ (F,Cl,OH)	0.898
Others			5.318
Total			100

Table 2. Mineral composition and content of the sample



Fig. 3. Modes of occurrence of iron, fluorine, rare earth and niobium, and distribution



Fig. 4. Elemental mappings of bastnaesite, monazite and columbite (a - Backscattering image of bastnaesite. b, c, d - Elemental mappings of Ce, La, F elements in bastnaesite. e - Backscattering image of monazite. f, g, h - Elemental mappings of Ce, La, Nd elements in monazite. i - Backscattering image of columbite. j, k, l - Elemental mappings of Nb, Mn, Fe elements in columbite)

3.1.3. Main minerals dissemination characteristics

Magnetite was the most important iron minerals in the ore. As shown in Fig. 5, the interparticle disseminated forms of magnetite are diverse, which show a relation to almost all minerals in the ore. In particular, magnetite was most closely associated with ankerite, often in an irregular shape, and the particle size was mainly distributed in -0.030 mm.

Fluorite was the primary F-bearing mineral in the ore. As shown in Fig. 6, the fluorite in the ore was veined and patched disseminated, often with ankerite and magnetite associated, the particle size was mainly distributed in -0.030 mm, fine grained fluorite was often wrapped by ankerite.

The main rare earth minerals in the ore were bastnaesite and monazite. As shown in Fig. 7, the bastnaesite was irregular, granular or long disseminated, mainly with ankerite and fluorite associated, fine grain grade was often inclusion of ankerite, disseminated particle size was mainly distributed in - 0.030mm. As shown in Fig. 8, the monazite was mainly irregular disseminated, often with ankerite and fluorite associated. The particle size distribution of monazite was mainly at -0.030mm, and the particle size distribution of inclusion distributed was at -0.010mm.

Columbite was the primary Nb-bearing mineral in the ore. As shown in Fig. 9, the columbite was disseminated in columns between iron ankerite, biotite, magnetite and apatite grains, with flat contact surfaces and the particle size mainly distributed at -0.030mm.



Fig. 5. Dissemination characteristics of magnetite



Fig. 6. Dissemination characteristics of fluorite



Fig. 7. Dissemination characteristics of bastnaesite



Fig. 8. Dissemination characteristics of monazite

3.2. Benefication evaluation of the sample

3.2.1. Separation of iron minerals

According to the mineralogical characteristics of the ore, the main minerals useful minerals magnetite, fluorite, bastnaesite, monazite and columbite disseminated in fine particle size, and uneven disseminated particle size, while the main gangue minerals ankerite to coarse disseminated, this difference in particle size was conducive to the use of stage grinding stage separation in the iron separa-



Fig. 9. Dissemination characteristics of columbite

tion process (Wang et al., 2018; Liu et al., 2014; Ge et al., 2009; Xiao et al., 2013). The first stage of operation adopted the stage crushing and stage dry magnetic separation to discard tailings, which can greatly reduce the amount of subsequent ore processing, improve the beneficiation efficiency. Magnetite had obvious magnetic differences with other useful minerals, and in order to improve the crushing and separation efficiency, the second stage adopted the roughing method of high-pressure roller mill and wet magnetic separation (Li et al., 2014). In order to improve the grade of iron concentrate, the separation method of stage grinding and stage low-intensity magnetic separation was adopted in the third stage. The separation process, test conditions and results of magnetite were shown in Fig. 10. It can be seen from Fig. 10 that in the iron concentrate the TFe grade was 65.40% with a distribution rate of 38.03%.

3.2.2. Separation of rare earth

Because of the fine size of the useful minerals, the wet magnetic separation tailings were screened, the screen hole size is 0.5 mm, the yield of the screening operation for the product on the screen was 15.81% with a REE grade of 2.96%, the product on the screen used as tailings, and the product under the screen was combined with the tailings of grindings and separation for REE separation. The REE separation was carried out by mechanical flotation method with NaSiO₃ as the inhibitor (dosage:1 kg/t), salicylhydroxamic acid as the collector (dosage:1 kg/t) and compound advanced alcohol as the frother (dosage:0.05 kg/t). The separation process and results of REE were shown in Fig. 11. Compared with the combined separation method of low-grade rare earth ore, the single flotation method had a simple process and high separation efficiency (Wang et al., 2021). It can be seen from Fig. 11 that in the REE concentrate the REE grade was 50.66% with a distribution rate of 62.73%. In addition, the REE grade of -0.030 mm particle size in the rare earth concentrate was 51.39% and the REE grade of -0.030 mm particle size in the rare earth concentrate was 51.39% and the REE grade of -0.030 mm particle size.

3.2.3. Separation of fluorite

REE flotation tailings contain a large amount of fluorite and therefore have a high economic value and should be comprehensively recovered. Fluorite was the only fluorine mineral that could form industrial deposits, and flotation was the most important separation method in the process of low-grade fluorite

ore (Gao et al., 2021; Kienko et al., 2012; Zawala et al., 2007). The results of the process mineralogy study showed that the fluorite in the ore was finely disseminated and therefore recovered using a stage-grinding stage- mechanical flotation method. To further improve the concentrate grade, acid leaching was performed on the flotation concentrate. The inhibitor used in the flotation process was NaSiO₃ and polymerized sulfate (dosage:1.2 kg/t and 1.8 kg/t) and the collector was modified oleic acid (dosage:0.9 kg/t). The acid leaching conditions were 5:1 liquid to solid ratio and 4h leaching time. The separation process and results of fluorite were shown in Fig. 12. It can be seen from Fig. 12 that in the fluorite concentrate the CaF₂ grade was 95.23% with a distribution rate of 40.34%. In addition, the CaF₂ grade of -0.030 mm particle size in the fluorite concentrate was 95.22% and the CaF₂ grade of -0.030 mm particle size in the fluorite tailings was 9.63%, with a significant enrichment of fluorite at the fine particle size.



Fig. 10. Separation flow-sheet and results of iron minerals



Fig. 11. Separation flow-sheet and results of REE



Fig. 12. Separation flow-sheet and results of fluorite

3.2.4. Separation of niobium minerals

The grade of Nb₂O₅ in the fluorite separation tailings was 0.091%. To recover this niobium resource, physical and chemical beneficiation methods were used. Pre-concentration was carried out using table, and the concentrate was grinding and then upgraded to Nb₂O₅ grade by magnetic separation, acid leaching and flotation. The inhibitors used in the flotation process were sodium fluorosilicate, lead nitrate and CMC (dosage:2 kg/t, 1.4 kg/t and 0.7 kg/t), and the collector was salicylhydroxamic acid (dosage:2 kg/t). The acid leaching conditions were 5:1 liquid to solid ratio and 5h leaching time. The separation process and results of niobium minerals were shown in Fig. 13. It can be seen from Fig. 13 that in the niobium concentrate the Nb₂O₅ grade was1.631% with a distribution rate of 5.56%.

The fine particle size of the niobium mineral disseminated was the main reason for the unsatisfactory separation effect. Fig. 14 shows the SEM image of columbite disseminated in ilmenite, the columbite disseminated particle size was less than 0.010 mm, and it was completely included by ilmenite. If further grinding makes the niobium mineral single liberated, it will cause the ore argillization phenomenon, and the microfine particle size has a greater impact on the separation effect.



Fig. 13. Separation flow-sheet and results of niobium minerals



Fig. 14. Microfine grained columbite was disseminated in ilmenite

4. Conclusions

The rare earth wall rock contain small amounts of iron, rare earth, fluorine and niobium elements, which were mainly occurrenced in minerals, Fe (Magnetite), REE (Bastnaesite and Monazite) and niobium (Columbite), and were uniformly distributed within the occurrence minerals. The useful minerals were closely disseminated with ankerite, mostly in inclusions, and the disseminated particle size was generally fine, mainly distributed in -0.030 mm particle size, and single liberation was difficult.

The magnetic separation in the stage grinding stage can effectively separation the magnetite with uneven distribution of embedded size and fine size (TFe concentrate grade: 65.40%, distribution: 38.03%). In this process, the liberation efficiency of useful minerals was improved by the addition of a high pressure roller mill. Rare earth elements can be effectively recovered from the wall rock by single flotation (REE concentrate grade: 50.66%, distribution: 62.73%), and the process was simple. The grade of fluorite concentrate was increased to 95.23% by stage grinding stage flotation combined with acid leaching. The gravity concentration was less effective in treating the micro-fine grained columbite, and a large amount of columbite went into the tailings.

This study provides suggestions for the rational development and utilization of rare earth carbonate wall rocks and gives a reasonable level of recovery prediction. In addition, it can provide a reference for the development of the same type of ore resources.

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