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Study on fluoride fixation effect of Bayan Obo rare earth iron ore and three sodium agents under microwave irradiation

Jing Guo [1,2], Ming Wen [1], Jie Li [1], Xunhai Hong [1], Wenhao Zhang [1], Yonglun Wang [1]

[1] Key Laboratory of Integrated Exploitation of Bayan Obo Multi-Metal Resources, Inner Mongolia University of Science and Technology，Baotou 014010，China

[2] JINGNENG Holding Group, Datong 037300, China

Corresponding author: Wenming1869@163.com (Ming Wen)

Abstract: To investigate the fluorine fixation of Bayan Obo rare-earth iron ores in beneficiation and metallurgy processes, the effect of three sodium agents, namely, sodium hydroxide, sodium carbonate, and sodium bicarbonate, on fluorine fixation under the action of microwaves was investigated using X-ray diffraction, chemical detection, and orthogonal experiments. The effects of different types of sodium, roasting temperatures, sodium ratios, and roasting times on the fluorine fixation rate were evaluated. Results show that compared with conventional roasting, the fluorine fixation efficiency of Bayan Obo rare-earth iron ore under the action of microwave is superior after the formulation of the sodium agent, which is crucial for the study. Among the three sodium agents, the fluorine fixation effect of $NaHCO_3$ can be used as the preferred sodium agent. Orthogonal experiments showed that the factors influencing the magnitude of the fluorine fixation rate are the roasting temperature, sodium agent ratio, and roasting constant temperature time in the order of priority. The optimal conditions for the fluorine fixation process are the microwave roasting temperature of 973.15 K, sodium bicarbonate ratio of 40%, and roasting time of 60 min. The highest fluorine fixation rate of 86.72% can be obtained. The findings of this study can provide a reference for the development of green and economic recovery processes for Bayan Obo rare-earth iron ores.

Keywords: Bayan Obo rare earth iron ore, microwave roasting, sodium agent fluoride fixation

1. Introduction

The mineralogy of Bayan Obo ore is characterized by multiple elements, low ore grade (Chen and Yu, 1992; Hao et al., 2002; Liu et al., 2012; Ke et al., 2021; Hou et al., 2020; Tian, 2020), fine crystalline size of useful minerals in the ore and complex mineral composition structure (Omran et al, 2014; Ren, 2019; Opare et al. 2021). Due to the unique mineralogical characteristics of dolomite, both the "wet" rare earth enrichment process (Huang., 2000; Xu, 2005; Zheng, 2017) and the "carbon thermal roasting reduction-magnetic separation" process (Feng, 2017) produce a large amount of fluorine and sulphur containing polluting waste gas, causing serious environmental pollution (Wang et al., 2014; Kang et al., 2017). However, the importance of the evolution of the fluorine fixation reaction has not been taken into account in the traditional carbothermic reduction process (Xiao et al., 2015; Xue et al., 2021). Therefore, it is necessary to seek a green and efficient selection and smelting process. Studying the roasting method and optimization of fluorine fixation process is of great theoretical and practical significance for the enrichment of mineralogy knowledge and comprehensive utilization of mineral raw materials, and lays a certain foundation for the green environmental protection research of rare earth recovery technology and carbon thermal reduction technology in the future.

In recent years, many universities and scholars have conducted a lot of research as well as research and development of new processes in response to the problems in the existing processing and smelting production processes of Baosteel, seeking to find efficient, low-energy and green technical means. Li et

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al. (2014) proposed the use of "microwave-assisted heating low-temperature acid leaching" process to solve the problem of low recovery and high cost of dolomite in high-temperature acid leaching and roasting, with microwave-assisted heating to 220°C, acid-to-ore ratio of 1.5 and roasting for 8 min, the rare earth leaching rate increased to 92.55% and the acid leaching process time shortened. Zhang (2014) found that the fluorine generated in the sintering process of Bayan Obo iron ore concentrate formed gaseous fluoride with other constituents, and the degree of difficulty in the generation of each type of fluoride varied at different roasting temperatures, from easy to difficult for KF, NaF, SiF_4, MgF_2 and AlF_3, respectively. Li et al. (2016) characterised characterised the Bayan Obo rare earth iron ore concentrate before and after high temperature roasting and pointed out that fluorine in the mixed rare earth iron ore concentrate was mainly present in cerium fluorocarbon ($REFCO_3$), fluorspar (CaF_2) and apatite (Ca (PO_4) (F,Cl,OH)). After roasting, the microscopically tight mosaic relationship between fluorocerium ore and fluorspar can be disrupted and accompanied by the escape of HF.

In this study, Bayan Obo rare earth iron ore is heated and roasted under different conditions with the addition of different sodium agents to study the effect of sodium agent fluorine fixation under different conditions, and the best sodium agent fluorine fixation process parameters are calculated using orthogonal tests.

2. Experiment

2.1. Materials

The experimental raw material, Bayan Obo rare earth iron ore, was extracted from the main mine area of Bayan Obo and taken from Baosteel beneficiation plant, with a white-grey colour, and was ground in a mill, dried and sieved to a particle size of -0.074mm (>95%) and then analysed for chemical composition and XRD. The chemical composition of the minerals (mass fraction) is shown in Table 1 and the mineral XRD analysis is shown in Fig. 1., From the results, it can be seen that the test mineral powder contains a large variety of elements and has a high content of harmful elements fluorine, phosphorus as well as sulphur, with the mass fraction of fluorine being 11.32%. From the XRD diffraction analysis, it can be seen that the minerals contained in the test powder mainly include magnetite, hematite, fluorocerium, fluorite, and quartz. The sodium hydroxide, sodium carbonate, sodium bicarbonate and other reagents used in the test were all analytically pure.

Table 1. Chemical Constituents (Mass Fraction) of Bayan Obo Rare Earth Iron Ore，%

TFe	FeO	REO	Nb_2O_5	MnO	TiO_2	SiO_2	CaO	F	P	S
28.34	7.89	7.28	0.11	1.08	0.43	10.39	23.32	11.32	0.87	1.32

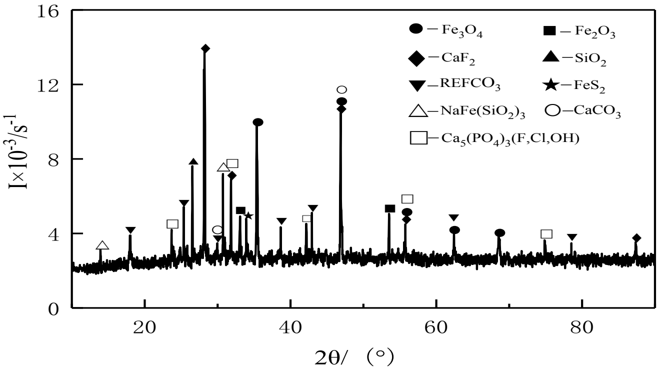


Fig. 1. XRD pattern of Bayan Obo raw ore

2.2. Experimental equipment

Main instruments: PULVERISETTE type planetary high energy ball mill, roasting equipment selected HY-ZG1512 microwave muffle furnace & macro thermogravimetric analyser, TE2010-LBSA124S electronic balance, JB-10 electromagnetic stirrer (B620 stirring bar), scanning electron microscope

(Panaco, Netherlands), D8ADVANCE type X-ray diffraction analyser, L5S type UV-visible spectrophotometer.

2.3. Experimental process

The samples (20g) were mixed with different proportions of NaOH, Na_2CO_3 and $NaHCO_3$ in a mixer, dried after mixing, placed in a crucible with a diameter of 80.0 mm, set different roasting temperatures and holding times (Table 2), heated and roasted in a microwave muffle furnace (4 kW), and then cooled down in the furnace, and the roasted minerals were placed in 250 mL of deionised water. After cooling, the roasted minerals were filtered by electromagnetic stirring at a speed of 200 r/min. Finally, filtrate and residue were obtained after 15 minutes of filtration. The experiment was done with only one variable, three parallel experiments were performed to avoid the human error caused by manual weighing, and the average of the three experimental results was taken.

Table 2. Experimental conditions

Species	Rosating temperature/K	Sodium ratio / %	Holding time/min
Scope	573~1073	5~50	30~80
Total	10	10	11

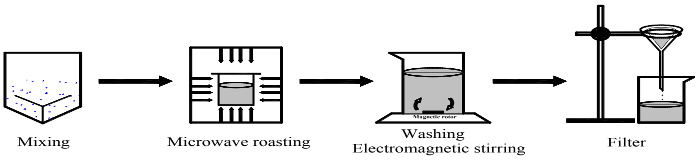


Fig. 2. Schematic diagram of experimental process and equipment

2.4. Analytical

In this experiment, orthogonal, single-factor experiments were used to measure the masses and calculate the weight loss before and after the experiments under different conditions, and the changes in the physical phase of the minerals before and after roasting were analysed using scanning electron microscopy and X-ray diffraction analyser. The weight loss rate is calculated according to the Eq (1);

$$C = \frac{\mathrm{M_a} - \mathrm{M_b}}{\mathrm{M}_a} \times 100\% \tag{1}$$

where M_a is the pre-experimental sample mass (g) and M_b is the post-experimental sample mass (g). The fluorine content can be measured spectrophotometrically according to the "Lambert-Bihl law". The experimental sample was mixed with phosphoric acid and perchloric acid in a water distillation flask and heated to about 140°C to separate the other interfering ions from the measurement process, after which the distillate was cooled and placed in an acetone medium solution and an acetic acid-sodium acetate buffer solution was added to adjust the pH value to about 5. The blank reagent was used as a reference and placed in a spectrophotometer at 620 nm to measure the absorbance of the test solution. A separate sample of the fluorine standard solution was taken and subjected to the above procedure. The fluorine content and absorbance were set as the horizontal and coordinates, respectively and a calibration curve was plotted. Based on the linear relationship between the fluorine content and absorbance of the test solution, the amount of fluorine was obtained and then calculated by Eq (2):

$$\omega(F) = \frac{V_0 \times m_0}{V_1 \times m_1 \times 10^6} \times 100\% \tag{2}$$

where, $\omega(F)$ is the percentage of fluorine by mass (%), m_0 is the fluorine content (μ m) obtained from the calibration curve drawn from the fluorine standard, m_1 is the sample volume (g), V_0 is the total volume of the fixing volume (mL), V_1 is the volume of the test solution taken (mL).

Letting $\rho(F)$ denote the rate of fluorine fixation after the addition of sodium agent to the solid, it follows that

$$\rho(F) = \frac{\omega(F)_1 \times M_1}{\omega(F)_0 \times M_0} \times 100\% \tag{3}$$

where, $\omega(F)_0$ denotes the percentage of fluorine mass of the original ore sample (%), $\omega(F)_1$ denotes the percentage of fluorine mass of the ore sample after roasting with sodium (%), M_0 denotes the mass of the original ore sample (g), M_1 denotes the mass of the ore sample after roasting with sodium (g).

2.5. Fluorine content versus absorbance curve

Using fluorine standard solutions to fix the volume. The following different concentrations of fluoride ion solutions were prepared separately, and after preheating the equipment, the absorbance of the above concentrations was measured by UV-visible in a 3 mL cuvette using a standard pipette, and the relationship between the concentration of the fluorine standard solution and the UV absorbance at 620 nm was determined as follows.

Table 3. Relationship between fluorine concentration and absorbance

Fluoride concentration(mg/L)	0.02	0.03	0.04	0.05	0.06	0.07	0.08
Absorbance（A）	0.020	0.026	0.034	0.042	0.050	0.057	0.065

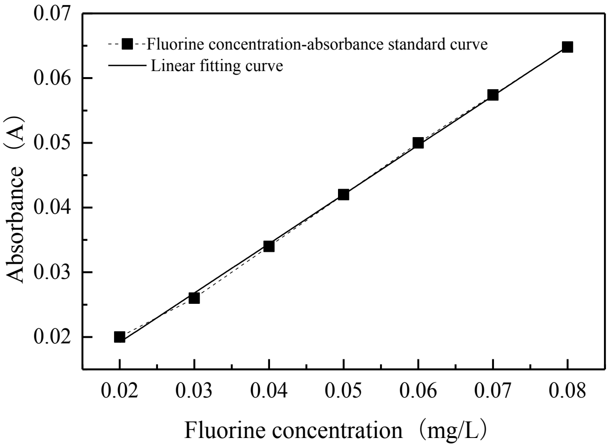


Fig. 3. Curve of fluorine concentration-absorbance relationship

Based on the relationship between the two, a linear fit gives the curve equation

$$Y = 0.7614X\ (R^2 = 0.9993) \tag{4}$$

where: Y is the absorbance (A) measured by the L5S UV spectrophotometer, X is the concentration of the fluorine standard solution (mg/L)

3. Results and discussion

3.1. Comparison of microwave roasting with conventional roasting for fluorine fixation

In order to compare the different behaviours of microwave and conventional roasting processes, dolomite and NaOH were mixed at a ratio of 10:1 in a crucible and heated at 773.15 K for 30 min in a microwave muffle furnace and a conventional muffle furnace, respectively. As seen from the results in Fig. 4 that the different heating methods roast the ore with different XRD pattern analysis results.

The XRD pattern shows that the roasted ore under conventional muffle heating is mainly composed of cerium fluorocarbon, fluorite, quartz, magnetite, sodium fluoride and rare earth oxides. The diffraction peaks of the reaction-produced roasted ore after microwave heating are weaker for cerium fluoride compared to the conventional roasted ore, while the diffraction peaks of sodium fluoride and rare earth oxides are stronger. This indicates that the decomposition of cerium fluorocarbon ore is more complete under this heating method and that it is easier to react with the sodium agent to form fluoride that does not readily escape into the air.

In summary, the use of microwave heating for solid fluoride experiments is of research significance. The reactions of the process can be summarised as follows:

$$6REFCO_3 \rightarrow RE_2O_3 + 3REOF + REF_3 + 6CO_2 \tag{5}$$

$$3REFCO_3 + 9NaOH \rightarrow 3RE(OH)_3 + 3NaF + 3Na_3CO_3 \tag{6}$$

$$2REFCO_3 + Na_3CO_3 \rightarrow RE_3O_3 + 2NaF + 3CO_2 \tag{7}$$

$$2CeFCO_2 + 3Na_2CO_2 + 1/2O_2 \rightarrow 2CeO_2 + 2NaF + 3CO_2 \tag{8}$$

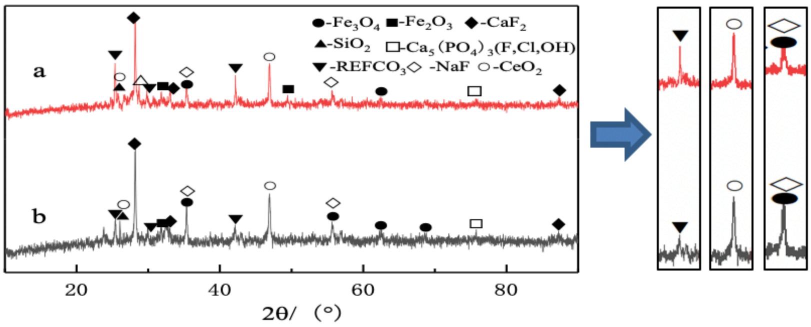
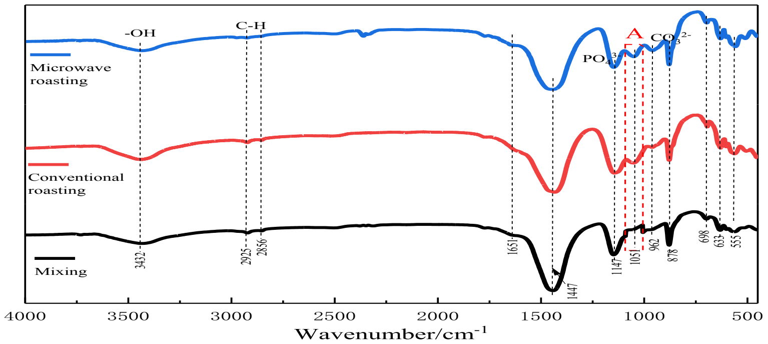


Fig. 4. XRD pattern (a. conventional roasting; b. microwave roasting method)

In order to study the changes of internal key structure of roasted minerals under different roasting conditions, the minerals cooled by the process were analyzed by FT-IR. The roasted minerals and potassium bromide were all mixed and ground at 1:150 to about 2 μm, and the tablets were weighed and quantified and placed in the Fourier transform infrared spectrometer. The wavenumber of infrared detection was set to 4000~400 cm^{-1}, the bin rate was set to 2 cm^{-1}, and the scanning speed was 2.5 kHz. The infrared spectral results obtained after atmosphere compensation were shown in Fig. 5.

Fig. 5. Infrared spectra of fluorine fixed minerals under different roasting conditions



The wavenumber at 3432 cm^{-1} corresponds to the –OH stretching vibration peak of the roasted mineral, that at 2925 and 2856 cm^{-1} are the asymmetric and symmetric stretching vibration peaks of the C–H bond of $-CH_2-$, respectively, and that at 1651 cm^{-1} is the bending vibration peak of $(OF)^{3-}$. The FT-IR diffraction peaks of $REFCO_3$ are located between 700 and 1500 cm^{-1} (Wen, 2016), and the specific corresponding wavenumbers are at 1446.7 and 878 cm^{-1}, reflecting the asymmetric stretching and in-plane bending vibration peaks of CO_3^{2-} in $REFCO_3$, respectively. The PO_4^{3-} group is found at 1148 and 961.7 cm^{-1}, and characteristic peaks of NaF are located at 1400 and 1051 cm^{-1} (Lin, 2020). The phosphate groups in the mineral are mainly $REPO_4$ and $Ca_5(PO_4)_3F$, and the bonding structure of CaF_2 located in the fingerprint region under different temperatures agrees well with the infrared profiles. Under the same conditions, the peak product and height can be analyzed more accurately based on the calculation of the infrared spectrum. To further illustrate the problem, focusing on the analysis of fluoride fixation products and changes in the fluoride fixation effect under different temperatures, the characteristic peak of sodium fluoride A band (1089.7–1001 cm^{-1}) was analyzed, and the different roasting temperature product bands were scaled up and placed in the same spectrum. In order to further explain this problem, the characteristic peak A of sodium fluoride (1089.7-1001 cm $^{-1}$) was analyzed under different roasting conditions, and the peak fitting quantitative analysis was carried out on the characteristic peak of sodium fluoride under the two conditions.

As Table 4 shows, by comparing the peak roasting conditions of the two groups of waves, it is obvious that the characteristic peak area (Fig. 6b) of sodium fluoride under microwave roasting is larger

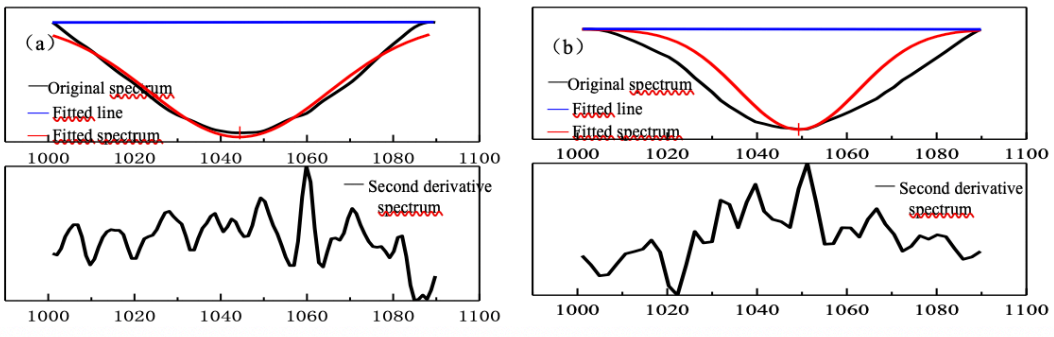


Fig. 6. Fitting spectra and second derivative spectra of fixed fluorine minerals in 1089.7-1001 cm^{-1} under conventional and microwave roasting conditions (a. conventional roasting; b. microwave roasting method)

Table 4. Fitting results in the wavenumber range of 1089.7–1001 cm^{-1}

Roasting conditions	Peak type	Peak position/ cm^{-1}	Peak height	Half tall wide/ cm^{-1}	Peak area
Conventional	Gaussian	1044	0.03838	48.922	1.91275
Microwave	Gaussian	1049	0.04644	43.852	2.12527

than that under conventional roasting condition (Fig. 6.a), and the peak fitting area of band 2 is 111.12% larger than that of band 1. By means of infrared spectrum analysis and peak value fitting, the results show that the fluorine fixation reaction is carried out and the fluorine fixation product sodium fluoride is generated, and the effect of microwave on fluorine fixation is better than that of conventional roasting.

3.2. Comparison of the fluoride fixation effect of different sodium agents

Without the addition of fluoride fixing agent in the roasting process of Bayan Obo rare earth iron ore, a large amount of hydrogen fluoride gas is generated, which pollutes the environment. With the addition of sodium as a fluoride fixing agent, the bastnaesite and some fluorspar in the roasted ore react with the sodium agent to form fluoride, which is "fixed" in the roasted ore, thus reducing the emission of hydrogen fluoride in the roasting environment. Three different sodium agents (NaOH, Na_2CO_3 and $NaHCO_3$) were used at 20% and the roasted ore was roasted at 773.15 K for 60 min to compare the XRD profiles.

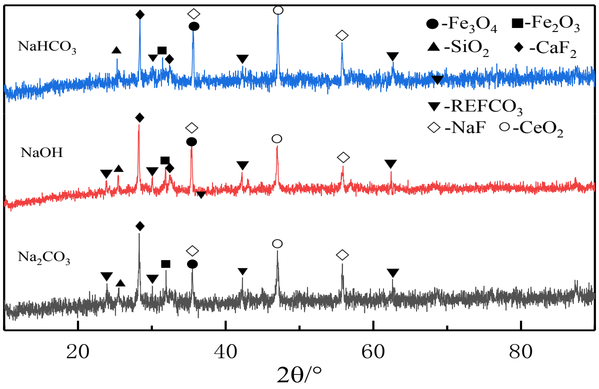


Fig. 7. Comparison of XRD patterns of Bayan Obo rare earth ore and ore roasted with different sodium fluoride fixer

According to the XRD diffraction pattern in Fig. 7, it is clear that the addition of different sodium fluoride fixing agents will have a different effect on the roasted minerals. Compared to the addition of NaOH and Na_2CO_3, when the roasted mineral of the $NaHCO_3$ sodium fluoride fixing agent was added, the peak number of cerium fluorocarbon is smaller. The addition of $NaHCO_3$ roasted minerals containing fluoride affords better decomposition and combined with the sodium agent to produce the fluoride fixing effect. The decomposition of cerium fluorocarbon to rare earth oxides (cerium dioxide) is evident from the XRD pattern, which reveals no or low fluoride peaks of the roasted minerals. It can be inferred that no new fluoride is produced and fluorine from the cracking of the roasted minerals is directly exhausted into the air as hydrogen fluoride. When the sodium fluoride fixing agent is added, the characteristic peak intensity of the fluoride (NaF) generated in the roasting environment is higher for the $NaHCO_3$ roasted mineral mix compared to Na_2CO_3, and the same is evident for the rare earth oxides (cerium dioxide), and these types of results occur because the water released from sodium bicarbonate in the roasting environment is conducive to the reaction compared to sodium carbonate, and water in the microwave environment as an active. The polar medium can promote decomposition reactions in the cerium fluorocarbon ore, thus reacting with sodium bicarbonate to produce non-volatile sodium fluoride, thus achieving the desired fluorine fixation effect. The XRD patterns of the rare earth oxides of the roasted minerals with the addition of NaOH were similar to those with the addition of $NaHCO_3$, suggesting that both achieved essentially equivalent fluoride fixation, but the addition of $NaHCO_3$ was more economically advantageous.

In order to further quantify the difference in the fluorine fixation effect of different sodium agents, the three roasted ores were directly measured for fluorine content under the following experimental conditions: roasting temperature of 973.15 K, 40% of sodium agent, and roasting constant temperature of 60 min.

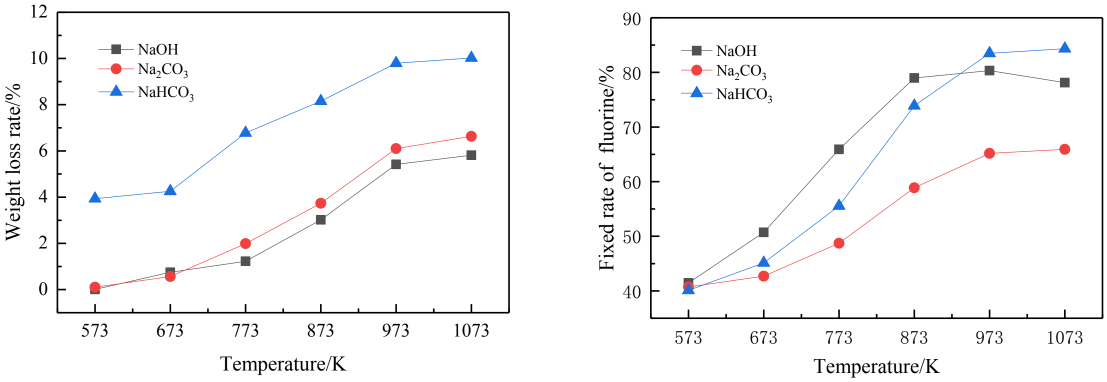


Fig. 8. Curve of weight loss rate and fluorine fixation rate of Bayan Obo rare earth iron ore roasting with different sodium agents changing with roasting temperature

From Fig. 8, it can be seen that the results of roasting weight loss rate and fluorine fixation efficiency differed under the same experimental conditions when different sodium agents (NaOH, Na_2CO_3 and $NaHCO_3$) were dispensed. At temperatures below 673 K, the rate of change of the fluorine fixation rate was basically unchanged because the fluorocerium cerium ore ($REFCO_3$) and fluorspar (CaF_2) in the Bayan Obo iron ore concentrate did not undergo decomposition reactions, and part of the weight lost was the surface free water contained in the ore powder as well as the mineral-bound water escaping from the water molecules during microwave heating, in addition to the decomposition reaction that occurred when $NaHCO_3$ sodium agent was added ($2NaHCO_3 \rightarrow Na_2CO_3+H_2O+CO_2$), so the weight loss rate is higher than that of minerals with NaOH and Na_2CO_3 sodium agents. After 673 K, the decomposition reaction of cerium fluorocarbon ore ($REFCO_3$) begins and is accompanied by the escape of HF, with the following chemical reaction equation:

$$REFCO_3 \rightarrow REOF + CO_2 \tag{9}$$

$$2REOF + H_2O \rightarrow RE_2O_3 + HF \tag{10}$$

At the same time, as the microwave roasting temperature rises, the close inclusions of fluorocerium ore ($REFCO_3$) and fluorspar (CaF_2) are cleaved, breaking the original atomic structure of the mineral and decomposing completely at around 973.15 K. According to numerous experimental findings, the following reactions occur in this temperature range for minerals with different sodium agents added:

$$3\text{REFCO}_3 + 9\text{NaOH} \rightarrow 3\text{RE(OH)}_3 + 3\text{NaF} + 3\text{Na}_2\text{CO}_3 \tag{11}$$

$$\text{REPO}_4 + 3\text{NaOH} \rightarrow \text{RE(OH)}_3 + \text{Na}_3\text{PO}_4 \tag{12}$$

$$\text{CaF}_2 + 2\text{NaOH} \rightarrow \text{Ca(OH)}_2 + 2\text{NaF} \tag{13}$$

$$2\text{REPO}_4 + 3\text{Na}_2\text{CO}_3 \rightarrow \text{RE}_2\text{O}_3 + 2\text{Na}_3\text{PO}_4 + 3\text{CO}_2 \tag{14}$$

$$\text{CaF}_2 + \text{Na}_2\text{CO}_3 \rightarrow 2\text{NaF} + \text{CaCO}_3 \tag{15}$$

$$\text{CaF}_2 + \text{Na}_3\text{PO}_4 \rightarrow 2\text{NaF} + \text{NaCaPO}_4 \tag{16}$$

$$2\text{REFCO}_3 + \text{Na2CO}_3 \rightarrow \text{RE}_2\text{O}_3 + 2\text{NaF} + 3\text{CO}_2 \tag{17}$$

$$2\text{REFCO}_3 + 2\text{NaHCO}_3 \rightarrow \text{RE}_2\text{O}_3 + 2\text{NaF} + 4\text{CO}_2 + \text{H}_2\text{O} \tag{18}$$

$$\text{CaF}_2 + \text{NaHCO}_3 \rightarrow 2\text{NaF} + \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \tag{19}$$

$$2\text{REPO}_4 + 6\text{Na}_2\text{CO}_3 \rightarrow \text{RE}_2\text{O}_3 + 2\text{Na}_3\text{PO}_4 + 3\text{H}_2\text{O} + 6\text{CO}_2 \tag{20}$$

$$\text{CaF}_2 + \text{Na}_3\text{PO}_4 \rightarrow 2\text{NaF} + \text{NaCaPO}_4 \tag{21}$$

In the initial stage of the temperature rise, the fluorine fixation efficiency of all three sodium agents showed an increasing trend and NaOH was more effective in fixing fluorine than the other sodium agents. This is mainly attributed to the reaction between the roasted minerals and the production of strong-base NaOH after decomposition. The resulting Na_2CO_3 can be used in the next step of the fluorine fixation process of sodium carbonate roasting. Furthermore, owing to the lower melting point of NaOH, the transformation of the roasted ore from the solid phase to the liquid phase promotes the reaction, thus reflecting the better fluorine fixation rate of NaOH in the initial stage compared with the other sodium agents. According to the analysis of the fluorine fixation effect of Na_2CO_3, with the increasing temperature, the rate of fluorine fixation gradually showed a decreasing trend, which may be due to the reaction of fluorite with the generated sodium fluoride at higher roasting temperature to produce $\text{Na}_x\text{REPO}_4\text{F}_x$, which is difficult to dissolve in water, affecting the fluorine fixation effect. When NaHCO_3 was added as the sodium agent, the fluorine fixation efficiency was 83.49% at 973.15 K, which visually reflected that the fluorine fixation effect was better than NaOH and Na_2CO_3, and also verified the results of XRD analysis. Therefore, NaHCO_3 was chosen as the preferred sodium agent for the fluorine fixation process and was used to carry out subsequent experiments.

3.3. Orthogonal and one-way experiments

The sodium fluoride fixing agent was NaHCO_3, and the orthogonal experiments were conducted to determine the effect of roasting temperature, constant temperature time and sodium ratio on the fluoride fixation rate during the roasting process, so as to provide a theoretical basis for the subsequent single-factor experiments. The design of the orthogonal experimental scheme and the experimental results are shown in Table 5.

Based on the experimental result data, the extreme difference analysis was done separately for three different temperatures. Firstly, at the roasting temperature of 573.15 K, the combined values of each level were calculated to be $\text{I}_{573.15}=122.39$, $\text{II}_{573.15}=169.9$ and $\text{III}_{573.15}=235$, then the average combined values of each level of this factor were: $K\text{I}_{573.15}=40.8$, $K\text{II}_{573.15}=56.63$, $K\text{III}_{573.15}=78.33$, then under the roasting temperature 573.15 K, the extreme difference is: $R_{573.15}= K\text{III}_{573.15}-K\text{I}_{573.15}=43.49$. Similarly, repeat the above process, respectively, to calculate the combined value of the level of each factor, the combined average and extreme difference values, as shown in Table 6. The magnitude of the extreme difference values represents the order of influence of this factor on the variation of the fluorine fixation rate compared to the other factors. According to Table 6, the extreme difference values are $R_{37.54}$ (roasting temperature) > $R_{7.16}$ (sodium ratio) > $R_{6.77}$ (roasting time), so the experimental process has the following order of influence on the fluorine fixation rate: roasting temperature, sodium ratio and constant temperature. The higher value of the extreme difference of temperature compared to the other two means that it has the greatest influence on the fluorine fixation rate in this process and should be given priority in the subsequent single-factor experiments, while the similar difference of the R-value of the sodium agent ratio and the roasting time indicates that they have a similar influence on the fluorine fixation rate in the fluorine fixation process. Using ANOVA, the fluoride fixation rate was calculated as shown in the Table 6.

Table 5. Orthogonal test scheme and experimental results

No.	Factor			Experimental result
	Roasting temperature/K	Sodium ratio /%	Roasting time/min	Fluorine fixation rate%
1	573.15	30	20	32.14
2	573.15	40	40	43.47
3	573.15	50	60	46.78
4	773.15	30	40	53.42
5	773.15	40	60	54.30
6	773.15	50	20	62.18
7	973.15	30	60	83.49
8	973.15	40	20	69.95
9	973.15	50	40	81.56
I	122.39	169.05	164.26	
II	169.9	167.72	178.45	
III	235	190.52	184.57	
K1	40.80	56.35	54.75	
K1	56.63	55.91	59.48	
K1	78.33	63.51	61.52	
R	37.54	7.6	6.77	

Table 6. Analysis of variance table

Factors	Variable sum of squares	Degrees of freedom	The proportion of F	The critical value of F	Significant
Temperature	2130.69	2	29.442	39	*
Accounted	109.17	2	1.508	9	
Roasting time	72.37	2	1.000	9	

The results show that $F_{0.025}$ (2,2) > F (firing temperature) > F (percentage of sodium) > F (firing time), with firing temperature having a significant effect on the fluorine fixation effect, followed by the percentage of sodium and firing time. This result is consistent with the results of the ANOVA.

3.3.1 Effect of microwave roasting temperature on fluoride fixation rate

According to the results of the orthogonal experiment, it can be seen that the microwave roasting temperature is an important factor affecting the fluorine fixation efficiency, in the single-factor experiment, the amount of $NaHCO_3$ is selected to be 30% placed in the microwave muffle roasting time of 50 min, the roasting temperature gradually increased from 623.15 K to 1073.15 K, the resulting roasted minerals were washed and filtered, and the effect of different roasting temperatures on the fluorine fixation rate and the weight loss rate after washing of dolomite with sodium agent was obtained. The effect of different roasting temperatures on the size of fluorine fixation rate and weight loss rate of iron ore concentrate after washing is shown in Fig. 9.

Fig. 9 (a) shows that the fluorine fixation reaction in roasting is divided into three stages: in the stage of 623.15-673.15 K, the fluorine fixation rate rises from 40.15% to 40.74%, which is a slow increase, while the weight loss rate of roasted minerals in this stage decreases with the increase of temperature after washing, and the main reason for the weight loss in the washing process is the washing away of the sodium agent ($NaHCO_3$) in the minerals, which means that the fluorine fixation reaction in this stage is not yet completely started. When the temperature is at 673.15-973.15 K, the fluorine fixation rate rises from 46.84% to 80.10%, which is an obvious increase. This indicates that this temperature range is the main stage of the fluorine fixation reaction; after the temperature rises to 973.15 K, the fluorine fixation rate of the roasted ore reaches 83.49%, after which the rate of increase begins to decrease with the increase in temperature. The solid fluorine reaction is no longer the main stage at this temperature.

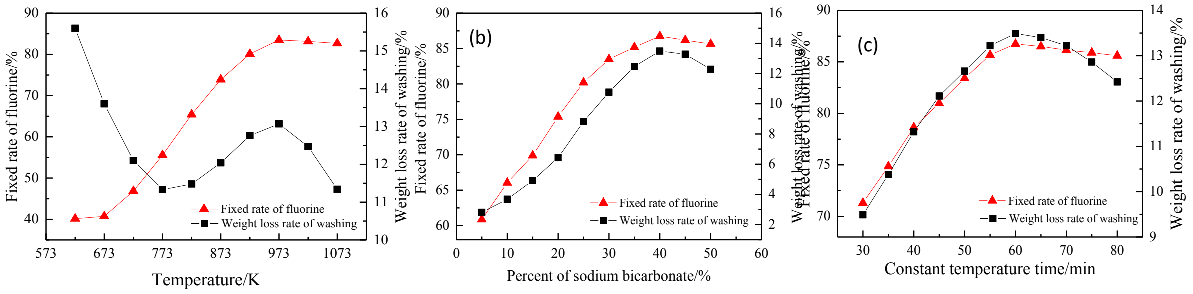


Fig. 9. Curve of weight loss rate and fluorine fixation rate of Bayan Obo rare earth iron ore roasting with different sodium agents changing with roasting temperature

In combination with the above discussion, 973.15 K was chosen as the preferred temperature for the fluorine fixation process and subsequent tests were carried out. From Fig. 9b, it can be seen that the addition of sodium carbonate affects the magnitude of the fluorine fixation results during the roasting of the raw dolomite. With the increase of $NaHCO_3$ dosage ratio, the fluorine fixation rate showed an increasing trend, when the $NaHCO_3$ dosage ratio reached 40%, the fluorine fixation rate reached 86.12% and the increase rate was obviously reduced, this situation is mainly due to the appropriate amount of sodium agent is conducive to the recovery of fluorine ions, when the $NaHCO_3$ dosage ratio is too little or too much, it is not conducive to the complete fluorine fixation reaction, according to the analysis of experimental results, when According to the analysis of experimental results, when the proportion of $NaHCO_3$ is 40%, the fluorine fixation effect is the best at this time. Fig. 9c shows that the fluorine fixation rate increases rapidly at the initial stage of microwave roasting thermostat (30-60 min); when the microwave roasting thermostat is heated to 60 min, it reaches a peak of 86.12%, and then the fluorine fixation efficiency starts to flatten and decreases slowly when the heating continues. The fluorocarbon cerium ore in the original Bayan Obo ore is thermally decomposed with the extension of the microwave roasting time, and the fluorine fixation reaction occurs between the cracking product and sodium carbonate to produce rare earth oxides and sodium fluoride, both of which have standard Gibbs free energy less than 0, which shows that the reaction is relatively easy to carry out thermodynamically, so the increase of the microwave roasting time can promote the complete reaction. However, the long roasting time will promote roasting similar to the sintering phenomenon, and this phenomenon increases the specific surface area of the material, hindering the reaction, the effect of sodium carbonate fluoride fixation is reduced, the roasted material will also be because of the particle size factor in the determination of fluoride ion concentration deviation, the need to grind treatment, increasing the process steps, so taking into account the process efficiency and economic efficiency, microwave roasting constant temperature suitable time selected is 60 min.

3.4. Characterisation of minerals after microwave roasting for fluorine fixation

3.4.1 BET specific surface area analysis

The main purpose of using the "microwave roasting - sodium fluoride fixation" technology to treat Bayan Obo rare earth iron ore is to study the green process in the recovery process. For roasted minerals, the size of the specific surface area directly affects the efficiency of the subsequent "leaching" of rare earths and "magnetic separation" of iron ore. The results of the orthogonal experiments showed that the roasting temperature is the most important factor affecting the size of the solid fluoride, so the ASAP2020M specific surface area analyser was used to analyse the specific surface area of Bayan Obo rare earth iron ore obtained at different roasting temperatures under the conditions of 40% sodium bicarbonate addition and roasting at a constant temperature of 60 min, as well as its specific surface area obtained by washing after cooling, the results of which are shown in Fig. 10.

According to Fig. 10, the BET surface area of roasted minerals decreases from 9.8 m^2/g to 0.81 m^2/g as the temperature increases from 573 K. When the roasting temperature is 573 K, the BET surface area of roasted tailings increases significantly compared to that of untreated minerals. It can be deduced that due to the different wave absorption properties of different minerals, a temperature difference between the different components of the mineral under the action of microwaves, resulting in a temperature

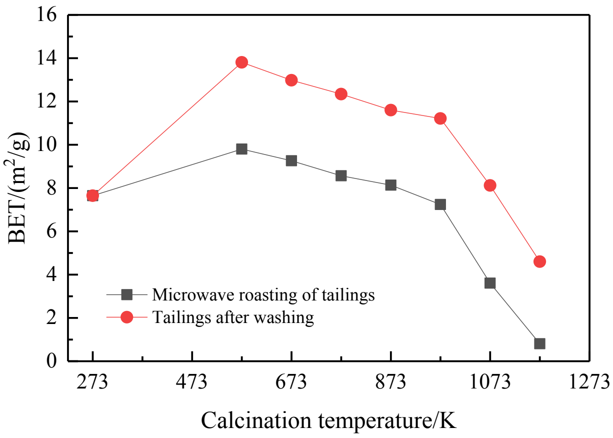


Fig. 10. Comparison of nitrogen absorption of two tailings at different roasting temperatures, i.e. BET specific surface area

gradient makes the mineral dissociate rapidly, increasing the specific surface area, in addition to the thermal decomposition of cerium fluorocarbon ore at this temperature is also an important reason for the increase in specific surface area. In the subsequent temperature range (i.e. the main temperature range for the fluorine fixation reaction), the reduction in specific surface area of the minerals reflects the significant sintering agglomeration of the minerals during the roasting and cooling process. The BET specific surface area of the minerals after microwave roasting with water washing showed a significant increase compared to the untreated minerals. It is worth noting that the specific surface area after water washing at 973.15 K is 1.47 times higher than that of the minerals before any treatment, a result that is clearly positive for improving subsequent beneficiation process conditions and reducing grinding costs.

3.4.2. SEM analysis

According to the macroscopic observation in Fig. 8, the morphology of rare earth iron ore after roasting mostly shows a loose structure. The thermal decomposition of cerium fluoride and calcium fluoride within the mineral and the fluoride fixation reaction are important reasons for the reduction in volume, increase in void space and the obvious pre and post morphological changes in granularity of the mineral after this process. Based on Fig. 8, the untreated dolomite rare earth ore is obviously large granular and has a smooth and dense surface, while the surface of the mineral after roasting by solid fluorine shows tiny particles and loose slit morphology. The cost of grinding in the subsequent process. Due to the complex composition of the Bayan Obo rare earth iron ore, the elements involved in the test were selected for face scan compositional analysis. From the surface scan observation in Fig. 11, it is known that the oxides of Fe and Ce are not uniformly distributed and have a common mosaic enrichment phenomenon, and the minerals obtained after the fluoride fixation process by microwave roasting of sodium agent, the surface of the oxides of Fe and the rare elements Ce are enriched with the generated sodium fluoride, this phenomenon is mainly due to the fluorine escaping from cerium fluoride ore in the microwave high temperature and sodium bicarbonate and attached to the surface of Fe and rare elements.

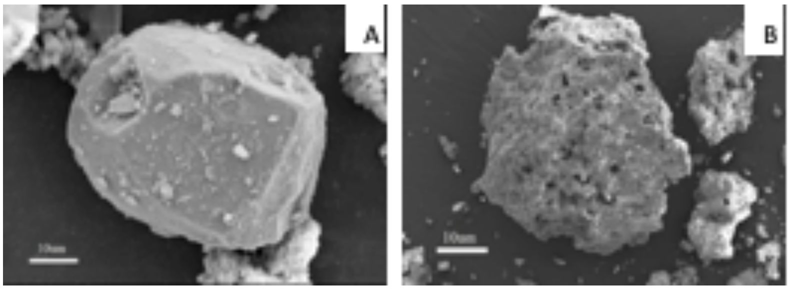


Fig. 11. SEM image of rare earth iron ore (A) and minerals after microwave fluorine fixation roasting (B) SEM - surface scanning

Fig. 12 shows the SEM-EDS morphological analysis results of the roasted fluorine fixation samples, it can be seen that the fluorine fixation roasted tailings of Bayan Obo rare earth iron ore mine have more and complex composition, the main minerals in the energy spectrum point A(1) and B(2) are hematite (Fe_2O_3), among which the energy spectrum point A(1) is accompanied by quartz (SiO_2), cerium fluoride ($REFCO_3$) and other mixtures, the SEM shows that Fe_2O_3 and SiO_2 are used as the internal matrix of the sample, while sodium fluoride and rare earth oxides are attached to the surface to form an aggregate, with a smooth and dense overall morphology, and the overall particles of the sample showing irregular characteristics. According to the SEM analysis, it was observed that the ore sample had a recrystallised form and a rare earth phase was present. CaF_2 does not decompose and react with sodium fluoride fixing agent under the test roasting temperature, so it does not affect the fluorine fixation rate.

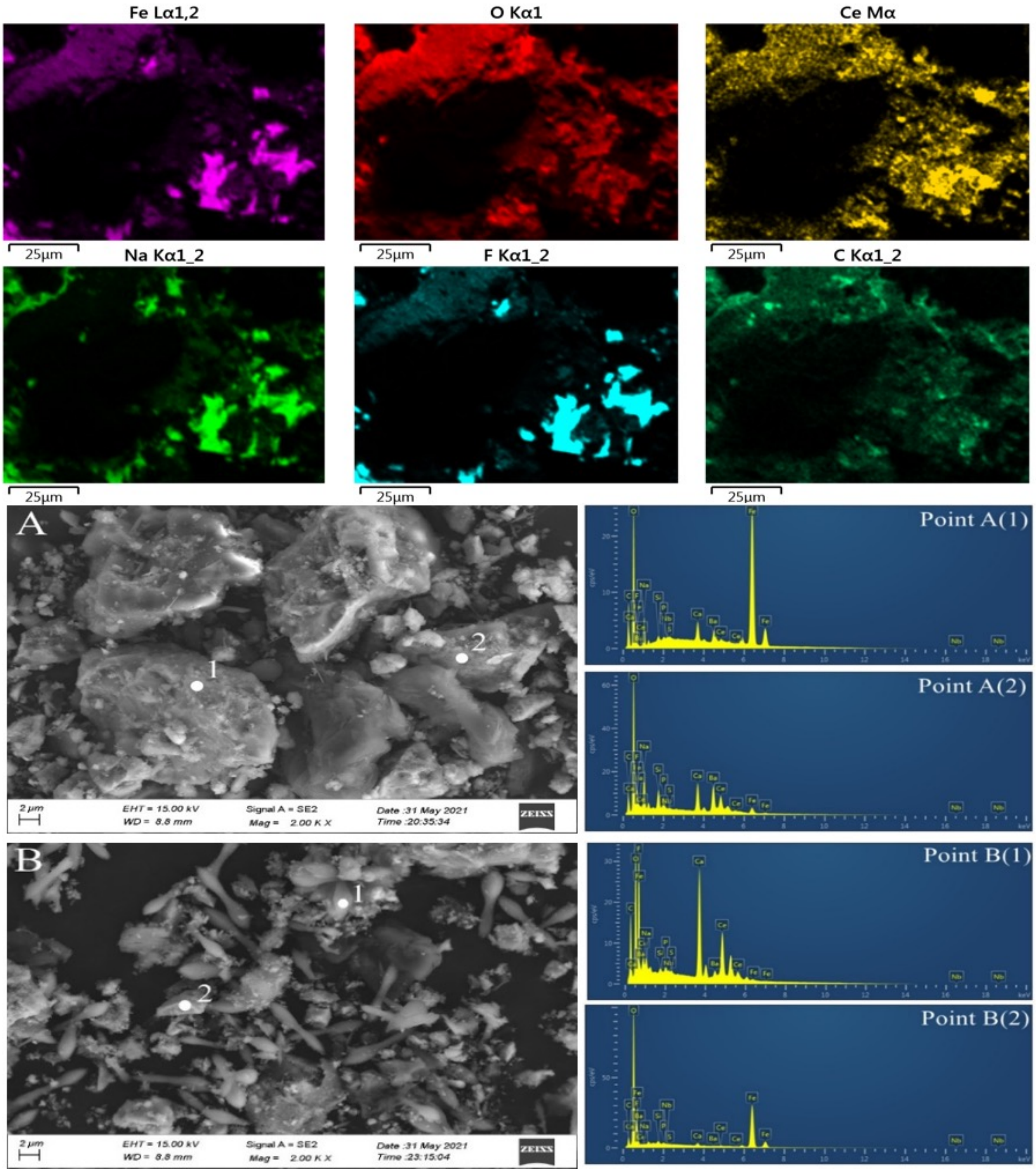


Fig. 12. SEM-EDS results for solid fluorine minerals

4. Conclusions

The effect of different sodium agents on the "fluorine fixation" of Bayan Obo rare earth iron ore in the microwave roasting process was investigated in the article, and the effect of different roasting temperature, sodium agent ratio and roasting constant temperature time on the fluorine fixation effect was analyzed by examining the index of fluorine fixation rate.

1. Compared with the conventional roasting method, the microwave roasting condition has better fluorine fixation effect of Bayan Obo rare earth iron ore with sodium agent.
2. The fluorine fixation effect of different sodium agents (NaOH, Na_2CO_3 and $NaHCO_3$) on the roasting of raw dolomite was different, and the fluorine fixation effect of $NaHCO_3$ was the best among the three sodium agents under the same experimental conditions.
3. According to the surface of the orthogonal experiment, the main and secondary factors affecting the fluorine fixation effect of Bayan Obo rare earth iron ore with the addition of the preferred sodium agent are: roasting temperature, sodium agent ratio, roasting time, and the best roasting process conditions are: roasting temperature 973.15 K, sodium agent dosage 40%, constant temperature time 60 min, and the optimum fluorine fixation rate of the roasted ore obtained is 86.12%.
4. Through microwave fluorine fixation roasting, the specific surface area of Bayan Obo rare earth iron ore increased to 1.47 times compared with the original ore during the pyrolysis and fluorine fixation washing process, and the roasted and washed minerals reflected the change from to large particles with smooth and dense surface to presenting tiny particles and loose slit morphology, which reduced the subsequent recovery process grinding cost.

The experimental results to study the optimization of roasting method and fluorine fixation process have important theoretical and practical significance for the enrichment of mineralogical knowledge and the comprehensive utilization of mineral raw materials, laying a certain foundation for the future green research of rare earth recovery technology and carbon thermal reduction technology, and having reference research value for the development of green and economic recovery process of Bayan Obo rare earth ore.

Acknowledgments

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