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Study on Escaping Fluorine Inhibition in Calcining Process of Mixed Rare Earth Concentrate*

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Abstract: GC technology was used to study escaping fluorine in calcined process of mixed rare earth concentrate. The mixed rare earth concentrate and it adding assistant of CaO-$NaCl$-$CaCl_2$ were calcined at 400 ~ 750 ℃ for 30 ~ 120 min, and then total amount of fluorine, exhausting ratio of fluorine, decomposition ratio and the component were determined. The results showed that adding CaO-$NaCl$-$CaCl_2$ the decomposition ratio was up to 90% at 700 ℃ in 1 h, and the escaping ratio of fluorine decreased from 29.52% to 0.948%. The average inhabitation ratio was 98.39%. This method supplied basis for low energy and clean decomposition of mixed rare earth concentrate.

Key words: mixed rare earth concentrate; CaO-$NaCl$-$CaCl_2$; roaste; fixed fluorine; GC technology
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The mixed rare earth concentrate is composed of bastnaesite and monazite. It mainly distributes in Baiyunebo, Inner Mongolia in China, and it contains 40% of positive ore of rare earth industry mineral of world. The proportion of bastnaesite and monazite in minerals is 9:1 ~ 1:1[1], and according to the analysis of minerals, this number becomes 6.5:3.5 in recent years[2]. Now sulfuric acid calcination and NaOH decomposition are the mainly used decomposition methods, but the problem of these two methods is environmental pollution. For this reason, the Na_2CO_3 calcination, NH_4Cl calcination, CaO calcinations, and etc. were studied and the purpose was to investigate the clean decomposition method[3~12]. In this paper, CaO and the molten salt of $NaCl$-$CaCl_2$ with low melting point was used to reduce the decomposing temperature, and GC technology was used to study the inhibitive effect on fluorine in process of mixed rare earth concentrate decomposed by CaO-$NaCl$-$CaCl_2$ with the aim to supply experimental basis for investigation of clean high efficiency technology.

1 Experimental

1.1 Experimental materials

The mixed rare earth concentrate was supplied by the Concentration Plant of Baotou Steel-Industry. The granularity of minerals was smaller than 0.074 mm, and the proportion of bastnaesite and monazite was 65.27:34.73. The chemical component is shown in Table 1. All reagents in the experiment were analytically pure grade.

1.2 Experimental process

The experiments were divided into gas absorption, derivatively gasification, and fluorine determination. The experimental equipments are shown in Fig.1.

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

Chemical composition	RE_xO_y	CaO	Si	T_{Fe}	P_2O_5	F
Content/%(Quality)	51.66	13.15	0.64	42.46	8.74	9.83

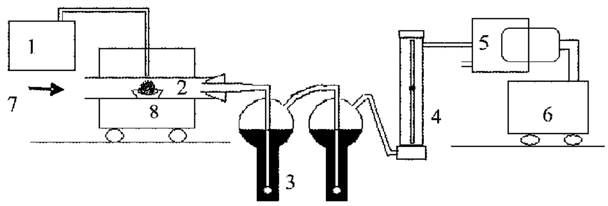

Fig.1　Installation of absorbing gas
1 – Temperature controller; 2 – Tube type resistance furnace; 3 – Glass plate absorber4 – Rotameter; 5 – Gas sampler; 6 – Cocurrent voltage-stabilized source; 7 – Air; 8 – Heating furnace

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Table 2 Experimental schemes

Time/min	Temperature/℃						
30	400	500	550	600	650	700	750
60	400	500	550	600	650	700	750
90	400	500	550	600	650	700	750
120	400	500	550	600	650	700	750

Mixed rare earth concentrate or it adding CaO-NaCl-$CaCl_2$ is put in a crucible which put in stainless steel tube, and is calcined for 1 h in heating furnace. The experimental schemes are shown in Table 2.

The gas containing fluorine produced in calcination process was absorbed by 50 ml 0.1 mol·L^{-1} NaOH solution, and the absorbing solution was derivatively gasified to determine fluorine by GC technology. Escaping ratio of fluorine in calcination process was calculated as following equation, escaping ratio(%) = the content of fluorine in gas phase/total content of fluorine in minerals. The decomposition ratio was determined by analyzing the calcined products. Its principle was that Ce in the mixed rare earth concentrate existed in Ce^{3+}, and Ce^{3+} was oxidized to Ce^{4+} during the decomposition of $CePO_4$ and $CeFCO_3$. The decomposition ratio(%) = $Ce^{4+}/\sum(Ce^{+3}+Ce^{+4})$.

2 Result and Discussion

2.1 Escaping regulation of flurorine in calcination process

2.1.1 Escaping regylation in calcinations process of mixed rare earth concentrate The mixed rare earth concentrate was calcined at 400 ~ 750 ℃ for 30, 60, 90, and 120 min. The environment humidity was 70%. The results are shown in Fig.2.

As shown in Fig.2, the escaping ratio of fluorine increases with the increasing of calcined temperature and time. The content of fluorine is low in calcined gas at 400 ℃, and the escaping ratio of fluorine is controlled by temperature, and it does not have obviously change with time at 500 and 550 ℃. When the temperature is up to 600 ℃, the escaping ratio of fluorine increases with the increasing of time which with temperature is the main effect on escaping fluorine. The experimental results show that the escaping ratio of fluorine is 29.952% at 750 ℃ in 120 min, when the environmental humidity is 70%. Base on this experimental parameter, the weight of escaping fluorine is 29.44 kg in calcination process of 1 t mixed rare earth concentrate, and it is 16.36 times higher than national standard.

2.1.2 Escaping regulation of flurine in process of the mixde rare earth concentrate calcined by CaO-NaCl-$CaCl_2$ In order to reduce the quantity of escaping flurine, the compared tests of mixed rare earth concentrate adding CaO-NaCl-$CaCl_2$ are performed, and the results are shown in Fig.3.

As shown in Fig.3, the escaping ratio of fluorine is also effected by time and temperature in process of mixed rare earth concentrate calcined by CaO-NaCl-$CaCl_2$. The escaping ratio of fluorine does not change with the increasing time and temperature obviously at 400 ~ 600 ℃, and the effect of temperature increases at 600 ~ 750 ℃. The escaping ratio of fluorine increases from 0.315% to 0.948% with the increasing of temperature from 700 to 750 ℃ in 2 h. At 700 and 750 ℃, the escaping ratio increases from 0.126% and 0.401% to 0.315% and 0.948% respectively, when the calcinations time increases from 30 to 120 min.

2.1.3 Analysis of two kinds of calcination process As shown in Figs.2 and 3, the escaping ratio of

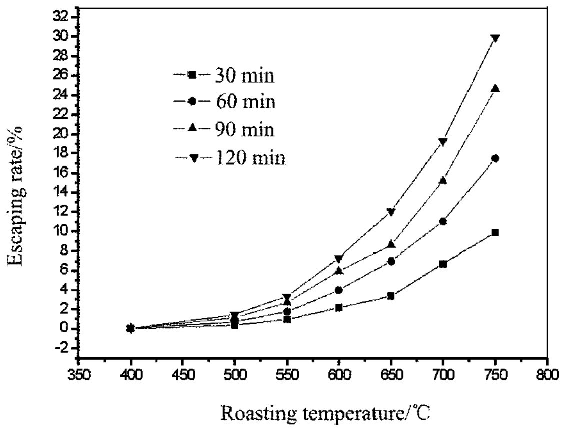

Fig.2 Effect of roasting time on overflowing ratio of fluorine in deferent temperature

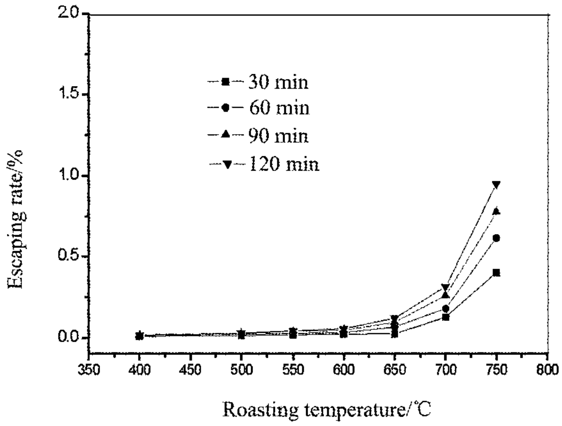

Fig.3 Relations of overflowing ratio of fluorine of mixed rare earth concentrate roasted with CaO-NaCl-$CaCl_2$ and temperature in deferent time

fluorine is obviously inhibited in process of mixed rare earth concentrate calcined by CaO-NaCl-$CaCl_2$ at the same condition. The results of Table 3 show that the average relative inhibiting ratio is 98.39% in 2 h. The escaping ratio of fluorine reduces from 29.925% to 0.948% at 750 ℃ in 120 min, and the relative inhibiting ratio is 96.83%. The weight of escaping fluorine is 0.93 kg in calcinations process of 1 t mixed rare earth concentrate, and it is far lower than national standard.

2.2 Decomposition reactions of calcined mixed rare earth concentrate

2.2.1 Decomposition reactions of calcined single mixed rare earth concentrate Refs.[11, 12] have studied calcination process of mixed rare earth concentrate. The results show the decomposition reactions as follows:

$REFCO_3 = REOF + CO_2\uparrow$ (1)

$Ce_2O_3 + 1/2O_2 = CeO_2$ (2)

$2REOF + H_2O = RE_2O_3 + 2HF\uparrow$ (3)

It is shown that mixed rare earth concentrate is decomposed to RE_2O_3 and REOF, and escapes CO_2 and HF. The fluorine of escaping gas is produced by REOF reacted with H_2O, and the reaction condition and regulation will be testified in comparing analysis of decomposition ratio and escaping regulation of fluorine.

The decomposition ratio of mixed rare earth concentrate is shown in Fig.4. As shown in Figs.2 and 4, the reaction is decomposition of bastnaesite at the humidity of 70%, when the temperature is lower than 600 ℃, and the reactions are shown as Eqs.(1) and (2). At 600 ~ 750 ℃, the reaction is escaping fluorin from REOF, and the reaction is shown as Eq.(3). In the process, monazite is not decomposed, and the decomposition ratio increases by Reaction (3) performed.

Table 3 Relative inhibiting effect adding assistant of CaO-NaCl-$CaCl_2$ at different temperature in 2 h

Calcining temperature/℃	Escaping ratio of fluorine from mixed rare earth concentrate/%	Escaping ratio of fluorine from mixed rare earth concentrate adding CaO-NaCl-$CaCl_2$/%	Relative inhibiting effect/%	Average relative inhibiting effect/%
500	1.476	0.027	98.17	98.39
550	3.360	0.043	98.72	
600	7.290	0.055	99.24	
650	12.078	0.119	99.01	
700	19.296	0.315	98.37	
750	29.952	0.948	96.83	

2.2.2 Decomposition reactions of mixed rare earth concentrate calcined with CaO-NaCl-$CaCl_2$ The process of mixed rare earth concentrate decomposed by CaO-NaCl-$CaCl_2$ has been investigated[13], and the results show that the decomposition reactions are as follows:

At 425 ~ 560 ℃, the reactions are as follows:

$REFCO_3 = REOF + CO_2\uparrow$

$Ce_2O_3 + 1/2O_2 = 2CeO_2$

$CaO + 2REOF = RE_2O_3 + CaF_2$ (4)

The monazite is decomposed at 630 ~ 700 ℃, and the reactions are as follows:

$3CaO + 2REPO_4 = RE_2O_3 + Ca_3(PO_4)_2$ (5)

$9CaO + CaF_2 + 6REPO_4 = 3RE_2O_3 + 2Ca_5F(PO_4)_3$ (6)

Compared with the results of 2.2.1, it is shown that adding CaO-NaCl-$CaCl_2$, monazite can be decomposed. Moreover, CaO reacted with REOF to fix the fluorine, and the results can be testified from the decomposition ratio and escaping regulation of fluorine.

In order to study the escaping condition of fluorine in the process of mixed rare earth concentrate decomposed by CaO-NaCl-$CaCl_2$, the decomposition experiment is supplemented, and the results are shown in Fig.5.

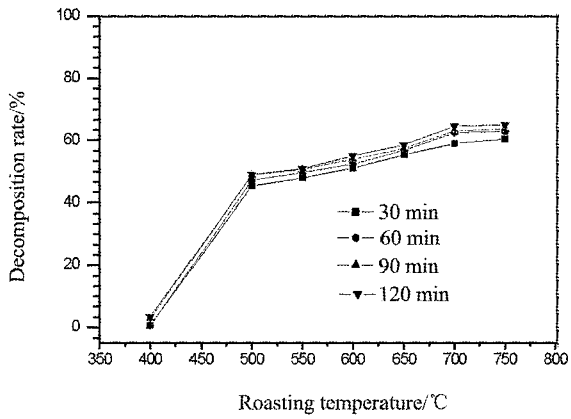

Fig.4 Effect of roasting temperature on decomposing ratio in deferent time

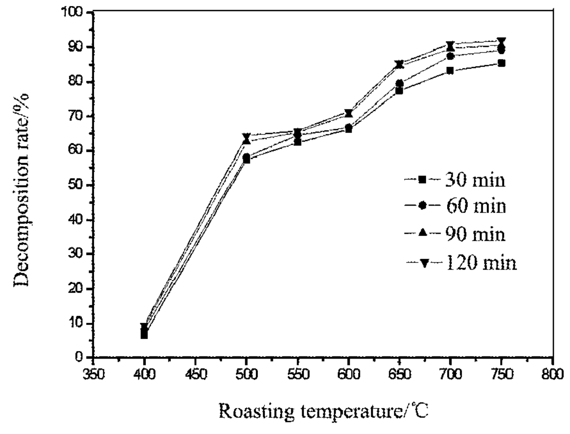

Fig.5 Effect of roasting time on decomposing ratio in deferent temperature

As seen in Figs. 3 and 5, the mixed rare earth concentrate adding CaO-NaCl-$CaCl_2$ has been decomposed at 400 ℃. The decomposition ratio is 9.5%, and the escaping ratio is 0.016% in 120 min. At 500 ℃, the decomposition ratio is 64.4%, and the escaping ratio of fluorine is 0.027%. The compositions of calcined product show that all the bastnaesite has been decomposed. The decomposition ratio do not change obviously at 500 ~ 600 ℃, and the monazite is not decomposed. The escaping ratio of fluorine reaches to 0.055% slowly which shows the obvious effect of fixed fluorine. The assistant of CaO-NaCl-$CaCl_2$ supplies the liquid phase which also reacts with monazite at 600 ~ 750 ℃, and the decomposition ratio increases again. The decomposition ratio reaches 91.92% at 750 ℃ in 120 min, and the escaping ratio is 0.948%. The main chemical reactions are Eqs. (2), (5) and (6) at 600 ~ 750 ℃[14~16].

It is also shown that the decomposition ratio of mixed rare earth concentrate added assistant does not have obviously change at 700 and 750 ℃ in 120 min, but at 750 ℃ the weight of escaping fluorine is 3.01 times higher than that at 700 ℃, and this reason need further investigation.

3 Conclusions

1. In the calcining process of the mixed rare earth concentrate, the escaping ratio of fluorine increased with the increasing temperature and time when the humidity was 70%, and the effect of temperature was obvious. The escaping ratio of fluorine was 29.925% at 750 ℃ in 120 min. The decomposition ratio was limited in content range of bastnaesite, and the monazite was not decomposed.

2. The fluorine eacaping was inhibited obviously in calcining process of mixed rare earth concentrate calcined by CaO-NaCl-$CaCl_2$. The average inhibited effect of fluorine reached 98.39% in 2h at different temperatures. The CaO-NaCl-$CaCl_2$ also increased the decomposition rate and reduce the decomposition temperature. The decomposition ratio was up to 90% at 700 ℃ in 120 min, and the relative inhibited effect of fluorine was 98.37%.

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