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Recovery of RE from Baotou rare earth concentrate with chlorination roasting①

SHI Wen-zhong(时文中)[1, 2], ZHU Guo-cai(朱国才)[1], HUA Jie(华 杰)[1, 3], XU Sheng-ming(徐盛明)[1], CHI Ru-an(池汝安)[1]

(1. Institute of Nuclear Energy Technology, Tsinghua University, Beijing 102201, China;
2. Chemistry Department, Zhumadian Teacher's College, Zhumadian 463000, China;
3. Department of Chemistry and Chemical Engineering, Yueyang Normal University, Yueyang 414000, China)

Abstract: A process for recovery of RE from Baotou rare earth concentrate was developed by fixing the fluorine and chlorinating RE with ammonium chloride in the ore. The optimum conditions were determined as follows: fixing the fluorine of the ore 80 min with the MgO dosage m (ore)/m (MgO)= 3∶1 at 600 ℃; chlorinating the fixed fluorine calcine 80 min, with NH_4Cl dosage m (NH_4Cl)/m (ore)= 2∶1 at 500 ℃. The RE recovery reaches 85% under optimum conditions. The products of fixing fluorine with MgO were determined by X-ray diffraction, and the mechanism of fixing fluorine was also discussed.

Key words: rare earth concentrate; fixing fluorine; chlorinating; rare earth

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1 INTRODUCTION

Baotou rare earth deposit is the largest one in the world. The concentrate is the mixture of bastnaesite ($REFCO_3$) and monazite ($REPO_4$) and the ratio of bastnaesite to monazite is generally 7∶3. The main processes to recover RE from the concentrate include the roasting with sulfuric acid, alkali heating process and high temperature chlorination etc[1]. The conventional processes produce waste acid, alkali or discharge gas to pollute the environment, therefore the metallurgists try to seek the green chemistry process with low cost, simple process and low pollution in recent years[2, 3].

Chlorinating RE of bastnaesite with NH_4Cl was invented by Tsinghua University[2, 4]. In this process, RE in the ore is chlorinated by HCl which is decomposed from NH_4Cl. Generally rare earth ore should be firstly defluorinated with Na_2CO_3 roasting, then the fluorine (NaF) is washed away with hot water before chlorinating RE with NH_4Cl. Actually the proposed process would also pollute the environment for containing fluorine wasting water. It should be further studied if the chlorinating process is suitable for the recovery of RE from the Baotou rare earth concentrate. To avoid generating containing-fluorine wastewater, MgO is selected to fix the fluorine of the rare earth concentrate in the calcine. After fixing-fluorine treatment, chlorinating RE with NH_4Cl roasting is further applied to concentrate.

The condition of fixing-fluorine and chlorination with NH_4Cl is determined in this investigation. The recovery of RE reaches 85% under the optimum conditions. The process of chlorination with NH_4Cl roasting has good selectivity to Fe, Al, Si and Th[5-12], and it simplifies the fluorine treatment of rare earth ore. Therefore the new process is favorable to purification and separation in recovery of RE. At the same time, the mechanism of fixing fluorine is also discussed based on the analysis of the products of the MgO reacting with the rare earth concentrate determined by X-ray diffraction.

2 EXPERIMENTAL

2.1 Materials

Baotou mixed RE concentrate is the main material used in this experiment. The chemical composition and the rare earth partitioning of the concentrate are listed in Table 1 and Table 2 respectively.

2.2 Principles

Magnesium oxide is used as de-fluorine agent in this experiment. The fluorine contained in the concentrate is turned into insoluable substances and there is no need to wash them away before

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Correspondence: Dr. ZHU Guo-cai, E-Mail: zhugc@mail.tsinghua.edu.cn

Table 1 Chemical composition of Baotou Mixed RE Concentrate (mass fraction, %)

Element	TREO	Ca	Mg	Fe
Content	52.1	9.0	0.15	2.0
Element	Al	Si	P	F
Content	0.12	0.030	0.25	7.15

Table 2 RE partitioning of Baotou Mixed RE Concentrate (mass fraction, %)

Component	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3
Content	24.4	51.4	5.5	16.6
Component	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7
Content	1.1	0.000 5	0.96	0.000 5
Component	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3
Content	0.001 0	0.000 3	0.000 5	0.000 3
Element	Yb_2O_3	Lu_2O_3	Y_2O_3	REO_T
Content	0.000 8	0.000 3	0.001 0	52.1

chlorinating roasting. After the fluorine in the concentrate is fixed, the calcine is then roasted with ammonium chloride and the RE are changed into water soluble chlorides, which can be leached with hot water. The reactions can be expressed as[9, 13, 14]:

$$NH_4Cl = NH_3 + HCl\ (328\ ℃) \quad (1)$$

$$RE_2O_3 + 6HCl = 2RECl_3 + 3H_2O \quad (2)$$

$$2CeO_2 + 8HCl = 2CeCl_3 + Cl_2\uparrow + 4H_2O \quad (3)$$

$$RE_2O_3 + 3Cl_2 = 2RECl_3 + O_2\uparrow \quad (4)$$

2.3 Experimental methods

10 g mixed RE concentrate was mixed with some amounts of de-fluorine agent in each experiment. The mixture was then roasted in muffle furnace to fix fluorine. The calcine was further mixed with NH_4Cl and then roasted again in muffle furnace at the designed temperature. The resulting calcine was leached with hot water. By analyzing the concentration of the leaching solution, the recovery of RE could be calculated.

2.4 Analysis methods

The chemical composition and RE partitioning of Baotou rare earth concentrate was analyzed with ICP. The concentration of rare earth in the leaching solution was analyzed by EDTA titration method to calculate the recovery ratio of RE. D/max-ⅢB X-ray diffractometer(tube voltage 35 kV, Cu target, integral time 0.2 s/step, speed 0.5 (°)/s) was used to determine the products of fixing fluorine calcine with MgO roasting.

3 RESULTS AND DISCUSSION

3.1 Determination of dosage of fixing fluorine reagent

To avoid forming rare earth fluoride and to improve the recovery of rare earth, the fixing fluorine reagent was added before recovery of rare earth by roasting the calcine with ammonium chloride. 30 g of rare earth concentrate with different dosages of MgO were roasted in each experiment. One-third amount of the resulting calcine was then chloridized with NH_4Cl and leached with water. The effect of the dosage of fixing fluorine reagent on the RE recovery is illustrated in Fig. 1. It achieved maximum with the MgO dosage m (ore)/m (MgO) = 3∶1 and decreased as the dosage of MgO increased. The reason is that excessive MgO would consume chlorinating agent NH_4Cl, then affect the chlorination of the rare earth of the concentrate.

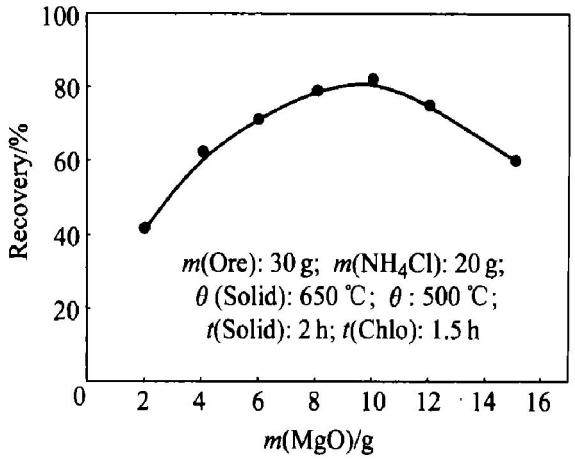

Fig. 1 Effect of fluorine-fixing reagent on recovery of RE

3.2 Effect of fluorine-fixing temperature on RE recovery

The effect of fluorine-fixing temperature on RE recovery is shown in Fig. 2. It shows that the optimum temperature is 600 ℃. Lower temperature is not favorable for the fluorine-fixing process. However, the recovery of RE will not increase significantly if fluorine-fixing temperature is higher than 600 ℃.

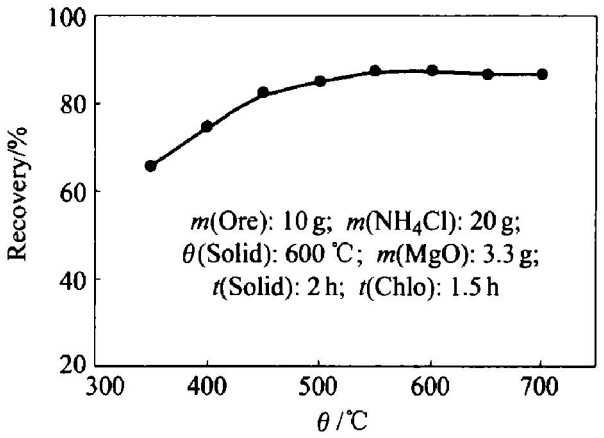

Fig. 2 Effect of fluorine-fixing temperature on recovery of RE

3.3 Effect of fluorine-fixing time on RE recovery

Actually the effect of roasting time of fixing-fluorine process is very small from the results in Fig. 3. It implies that the roasting process of fixing-fluorine time may be omitted, the fixing-fluorine and chlorination process could be combined into one step. Further investigation should be done for the combination of the fixing-fluorine and chlorination process though the recovery of rare earth reaches above 85% at the optimal roasting time 80 min.

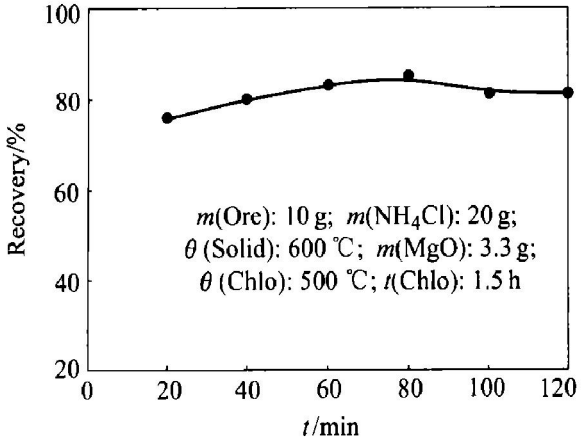

Fig. 3 Effect of fluorine-fixing time on recovery of RE

3.4 Effect of NH_4Cl amount on recovery of RE

Various amounts of NH_4Cl were added into the fluorine fixed calcine of the Baotou Rare Earth Concentrate. The mixture was then roasted for 1.5 h at 500 ℃. The relation between the RE recovery and the dosage of NH_4Cl is shown in Fig. 4. The results show that the recovery ratio of rare earth rises up to 85% when m (ore)/m (NH_4Cl) = 1∶2, and no obvious increase of RE recovery ratio is observed if more NH_4Cl is added.

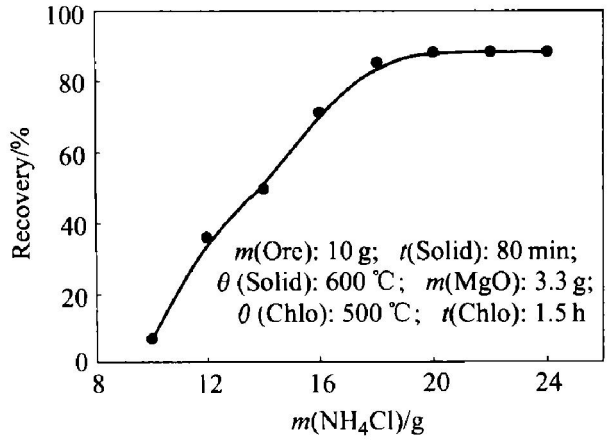

Fig. 4 Effect of dosage of NH_4Cl on recovery of RE

3.5 Effect of chlorination roasting temperature on RE recovery

When the chlorination roasting time was fixed for 1.5 h, the effect of roasting temperature on RE recovery ratio is shown in Fig. 5. It indicates that the RE recovery ratio increases with the increase of roasting temperature during 350-500 ℃, and the recovery ratio rises to the maximum at 500 ℃. However, the recovery ratio would decrease if the roasting temperature is further increased, this may be explained by the oxidation of the rare earth chlorides[6, 7].

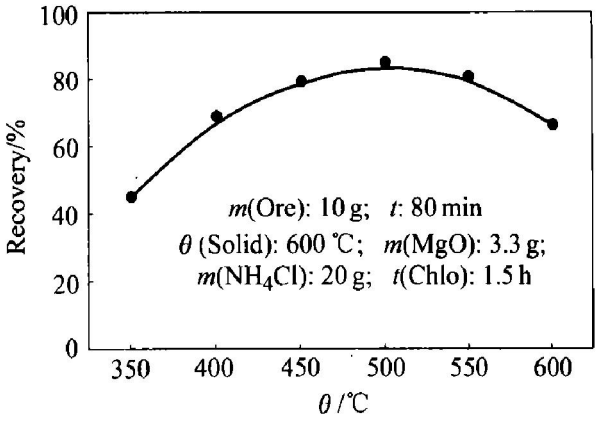

Fig. 5 Effect of chloridization temperature on recovery of RE

3.6 Effect of chlorination roasting time on RE recovery

The RE recovery ratio increases with the prolongation of roasting time at the initial stage, and then reaches its maximum. Nevertheless, the recovery ratio decreases if the roasting process continues. The most favorable roasting time is 80 min, see Fig. 6.

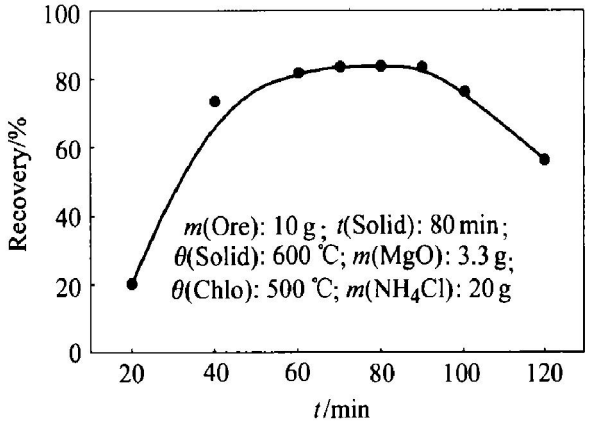

Fig. 6 Effect of chloridization time on recovery of RE

3.7 Mechanism of fluorine fixing process

The X-ray diffraction results of Baotou Mixed RE Concentrate, the fluorine-fixed calcine, and the leached gangue after chloridizing are shown in Fig. 7. It shows that the main phases in mixed RE concentrate are $CeFCO_3$ and $LaPO_4$, see Fig. 7(a); the main phases in fluorine-fixed calcine are La_2O_3, CeO_2, MgF_6 and Mg_2FPO_4, see Fig. 7(b), and the main phases in the leached gangue after chlorina-

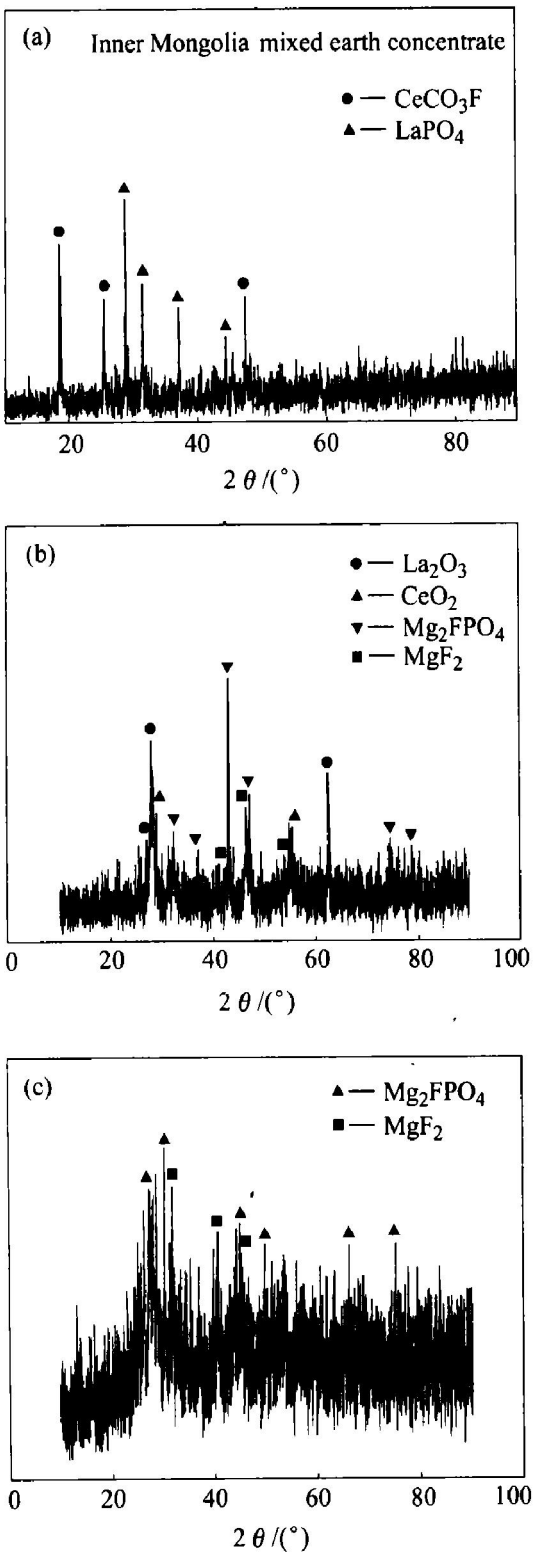

Fig. 7 X-ray diffraction patterns

tion are MgF_2 and Mg_2FPO_4, see Fig. 7(c).

From the above results, we can conclude that during the fluorine-fixing process of mixed RE concentrate, the fluorine in bastnaesite is turned into insoluble MgF_2, the PO_4^{3-} anion in the monazite is turned into $Mg(PO_4)_2$, which reacts further with MgF_2 to form the insoluble Mg_2FPO_4 at high temperature. Those reactions can be expressed as:

$$2REFCO_3 + MgO = MgF_2 + RE_2O_3 + 2CO_2 \uparrow \quad (5)$$

$$4CeFCO_3 + 2MgO + O_2 = 2MgF_2 + 4CeO_2 + 4CO_2 \uparrow \quad (6)$$

$$2REPO_4 + 3MgO = RE_2O_3 + Mg_3(PO_4)_2 \quad (7)$$

$$MgF_2 + Mg_3(PO_4)_2 = 2Mg_2FPO_4 \quad (8)$$

4 CONCLUSIONS

1) Fluorine-fixing chloridizing roasting is suitable for the recovery of RE from Baotou Mixed RE Concentrate. During this process, the de-fluorine calcine needs not to be washed, the reaction selection is excellent, there is no left acid in the RE leachate, and it contains little Fe, Si, Al and Th, which is favorable for further purification of leached rare earth solution.

2) The optimal fluorine fixing condition is that m (ore) : m (MgO) = 3: 1, de-fluorine temperature is 600 ℃, and de-fluorine time is 80 min. The optimal chlorination roasting conditions are that m (ore) : m (NH_4Cl) = 1: 2, roasting temperature is 500 ℃, and the roasting time is 80 min. The process reaches 85% recovery ratio of RE. The combination of the fluorine-fixing and the chlorination of RE should be further investigated.

3) X-ray diffraction results show that the products of fluorine fixing process of mixed RE concentrate are MgF_2 and Mg_2FPO_4.

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