Article ID: 1003－6326(2003)06－1454－05

Mechanism of chlorinating lanthanum oxide and cerium oxide with ammonium chloride①

ZHU Guo-cai(朱国才)[1], LI Fu-ping(李赋屏)[2], XIAO Ming-gui(肖明贵)[3]

(1. Institute of Nuclear Energy Technology, Tsinghua University, Beijing 102201, China;
2. Institute of Earth Science and Resource, China University of Geosciences, Beijing 100083, China;
3. Department of Civil Engineering, Guilin Institute of Technology, Guilin 541004, China)

Abstract: Using ammonium chloride (NH_4Cl) as a chlorinating agent, the effects of chlorinating temperature, chlorinating time and NH_4Cl dosage on chlorination of La_2O_3 and CeO_2, and the thermal decomposition of $LaCl_3 \cdot 7H_2O$ and $CeCl_3 \cdot 7H_2O$ were investigated. The results show that 80% of both La_2O_3 and CeO_2 can be chlorinated at 300 ℃ for 90 min, and have no advantage to chlorination of lanthanum and cerium oxides at higher temperature. The thermal decomposition of $LaCl_3$ and $CeCl_3$ is carried out to explore the mechanism of chlorinating lanthanum and cerium oxides. At the same time, the chlorination of lanthanum and cerium oxides is not devoted to the HCl decomposed from NH_4Cl, but to NH_4Cl directly taking part in the chlorination of La_2O_3 and CeO_2. The lanthanum and cerium oxides in chlorination firstly form intermediate LaOCl and CeOCl, and then transfer to $LaCl_3$ and $CeCl_3$, finally to La_2O_3 and CeO_2, respectively. The thermal decomposition analyses of $LaCl_3 \cdot 7H_2O$ and $CeCl_3 \cdot 7H_2O$ further prove the existence of the intermediates LaOCl and CeOCl. Therefore the chlorinating temperature and time should strictly be controlled when the lanthanum oxide and cerium oxide are chlorinated with NH_4Cl. And over-dosage of NH_4Cl should be also applied in the process of chlorination.

Key words: lanthanum; cerium; mechanism; chlorination; thermal decomposition

CLC number: TF 803.24; TF 845.6 **Document code:** A

1 INTRODUCTION

The light rare earth ores such as bastnasite and Beiyuneboite are the ones with lanthanum and cerium element as main component (the content of lanthanum and cerium> 85% (mass fraction)). Generally, the light rare earth ores are decomposed by acid or alkali, then the rare earth products could be further recovered[1, 2]. Some shortages exist in the conventional process of recovering rare earth, such as long flow-sheet, multi-transferring form of the rare earth and so on. Furthermore, the waste acid or alkali and gas emission such as HF, SO_2 produced by acid or alkali would pollute environment. In order to resolve above problems, an alternative process of selective chlorination and recovery of rare earth was put forward[3-7]. The novel process can directly transfer the rare earth of the ore to rare earth chloride without multi-transferring form of rare earth elements, and be favorable to the environment due to no use of acid or alkali. At the same time, the selective chlorination would decrease the dissolution of impurities such as Fe, Al, Si and Th, so it would simplify the purification process of recovering rare earth. Furthermore, lanthanum and cerium are the main rare earth element components of light rare earth ore, and cerium can exist as trivalence or tetravalence. CeO_2 could not be dissolved in hydrochloric acid[8]. It is clear that the chlorination of lanthanum and cerium would directly affect the total recovery of rare earth for light rare earth ores. In this work, ammonium chloride is considered as an alternative to chlorinate lanthanum oxide and cerium oxide. The mechanism of chlorinating and the thermal decomposition of $LaCl_3 \cdot 7H_2O$ or $CeCl_3 \cdot 7H_2O$ are the focus in this study.

2 EXPERIMENTAL

The La_2O_3, $LaCl_3 \cdot 7H_2O$, CeO_2 and $CeCl_3 \cdot 7H_2O$ used in the experiment were analytically pure, and NH_4Cl used as a chlorinating agent was chemically pure. The experiments of La_2O_3 and CeO_2 chlorination were carried out in a muffle furnace. In each experiment, 1 g CeO_2 or 1 g La_2O_3 was mixed homogeneously with different amount of NH_4Cl, and then transferred to a capped pot. As the temperature of muffle furnace reached the assigned temperature, the capped pot was put into the muffle furnace, and roasted for a certain time. The calcine was leached with water, and filtered to get leach liquid. The

① **Foundation item:** Project(59804004, 50274046) supported by the National Natural Science Foundation of China

Received date: 2003－01－25; **Accepted date:** 2003－05－17

Correspondence: ZHU Guo-cai, PhD, Associate professor; Tel: +86-10-89796082; E-mail: zhugc@mail.tsinghua.edu.cn

La^{3+} and Ce^{3+} concentration of the leached liquid were determined with EDTA volumetric method. Based on the volume and concentration of the leached liquid, the chlorinating ratio of La_2O_3 and CeO_2 could be calculated. The thermal decomposition experiments of $LaCl_3 \cdot 7H_2O$ and $CeCl_3 \cdot 7H_2O$ were carried out at Universal DSC-2910 TA Instrument (Japan).

3 RESULTS AND DISCUSSION

3.1 Chlorination of La_2O_3 and CeO_2

When anhydrous mixed rare earth chloride is prepared, NH_4Cl as a chlorinating agent is applied to chlorinate mixed rare earth oxide[8-10]. Actually, it is the HCl from NH_4Cl that chlorinates the mixed rare earth oxide. The main chemical reactions are represented as follows:

$$NH_4Cl \xrightarrow{328\ ℃} NH_3 + HCl \quad (1)$$

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

All the trivalence rare earth elements, such as La_2O_3 and Ce_2O_3, can be described by reaction (2). For the tetravalence CeO_2, it was reported that the cerium chloride would be formed by CeO_2 reacting with the HCl decomposed from NH_4Cl, and the reactions can be expressed as follows[11]:

$$2CeO_2 + 2HCl = Ce_2O_3 + Cl_2 + H_2O \quad (3)$$

$$Ce_2O_3 + 6HCl = 2CeCl_3 + 3H_2O \quad (4)$$

$$Ce_2O_3 + 3Cl_2 = 2CeCl_3 + 3/2O_2 \quad (5)$$

To investigate the chlorination of La_2O_3 and CeO_2 by NH_4Cl, 1g La_2O_3 or CeO_2 is mixed with NH_4Cl at different ratio and roasted in a muffle furnace. The calcine is dissolved in water and filtered to get leaching liquid. By analysis of the La^{3+} or Ce^{3+} concentration in the filtered solution, the chlorinating rate of lanthanum and cerium oxides (α_{La} and α_{Ce}) can be calculated. The effects of mole ratio of NH_4Cl to rare earth oxide ($n = x_{NH_4Cl}/x_{La_2O_3}$ or x_{NH_4Cl}/x_{CeO_2}), roasting time and roasting temperature on the chlorination are shown in Tables 1 and 2.

The results in Tables 1 and 2 show that chlorinating rate of La_2O_3 or CeO_2 can reach about 80% at $n = 6$, $t = 15$ min and $\theta = 300$ ℃ for La_2O_3; and $n = 12$, $t = 90$ min and $\theta = 300$ ℃ for CeO_2 respectively. To illustrate the law visually, the relationship between the Ce chlorinating rate and chlorinating time for $n = 3$ and 12 in Table 2 is plotted, as shown in Fig. 1. It clearly indicates that the chlorinating rate of cerium increases with increasing chlorinating time for $n = 3$ at 300 ℃, and appears peaks chlorinating rate at 350 ℃ for 60 min and at 400 ℃ for 45 min. The chlorinating rate of cerium decreases with increasing chlorinating time for the experiments at the reaction temperature of 450 ℃ or higher. But the maximum chlorinating rate is less than 40% for the experiments of $n = 3$. For the experiments of $n = 12$ the chlorinating rate of cerium increases with increasing chlorinating time at 300 ℃. And the chlorinating rate reaches about 80% at 90 min. At 350, 400 and 450 ℃, the chlorinating rate decreases with increasing chlorinating time after it reaches the maximum. At the higher temperature, the time to reach maximum chlorination rate is shorter, and the total chlorinating rate is decreased. Since the chlorination of CeO_2 and the thermal decomposition of $CeCl_3$ are simultaneously existed, too high temperature or too long reaction time may make the $CeCl_3$ be decomposed. Therefore attention should be specially paid that the maximum chlorinating rate appears at below 300 ℃. At the same time, the chlorinating rate of lanthanum reaches 78% and that of cerium reach 50% at 250 ℃. The phenomenon is obviously against saying that the decomposition of NH_4Cl only occurs at temperature higher than 328 ℃. Therefore, in the chlorination of La_2O_3 and CeO_2 in heating NH_4Cl system, not only the decomposed HCl but also the NH_4Cl take part in the chlorinating reaction with process as follows:

$$La_2O_3 + 2NH_4Cl = 2LaOCl + 2NH_3 + H_2O \quad (6)$$

Table 1 Results of chlorinating La_2O_3 by NH_4Cl at different roasting time

θ/ ℃	n	α_{La}/ %				
		15 min	30 min	45 min	60 min	90 min
200	3	3.2	9.9	9.8	9.4	8.4
	6	6.0	15.8	26.6	17.8	15.8
	9	9.9	30.2	38.3	19.3	17.0
	12	10.8	44.3	40.2	31.6	30.2
250	3	32.3	24.3	50.4	51.2	53.2
	6	37.3	36.7	53.2	78.4	77.7
	9	39.1	50.8	68.5	75.7	75.2
	12	46.0	52.2	71.7	71.3	69.8
300	3	57.3	59.9	58.1	65.9	66.5
	6	80.2	80.0	81.2	79.9	79.5
	9	78.6	78.2	77.0	81.0	81.7
	12	70.2	74.2	83.5	82.3	81.9
350	3	59.8	70.2	77.4	70.5	70.1
	6	79.1	80.1	81.9	81.7	79.6
	9	79.4	82.1	80.1	80.8	81.2
	12	79.6	82.1	80.2	82.1	82.4

Table 2 Results of chlorinating CeO_2 by NH_4Cl at different roasting time

θ/ ℃	n	α_{Ce}/ %				
		15 min	30 min	45 min	60 min	90 min
250	3	3.8	6.8	15.2	19.9	24.2
	6	6.6	10.7	25.0	28.8	35.2
	9	9.8	13.6	28.7	30.3	50.8
	12	9.9	17.4	34.0	48.8	52.2
300	3	12.1	18.8	22.3	28.0	37.9
	6	25.7	32.7	40.3	60.3	62.5
	9	37.7	44.5	58.4	65.9	70.2
	12	49.8	57.8	68.8	77.9	79.9
350	3	8.5	15.3	17.8	22.4	11.5
	6	15.5	21.4	34.7	43.2	42.2
	9	34.1	46.6	45.8	51.7	59.9
	12	52.8	54.5	64.5	59.5	68.9
400	3	11.4	12.7	14.4	13.3	0.2
	6	35.1	36.9	41.2	37.2	17.4
	9	41.7	46.5	58.5	45.4	34.7
	12	43.6	51.7	68.7	61.4	55.3
450	3	7.3	1.1	0.3	0.3	0.2
	6	33.8	18.8	12.1	6.6	0.2
	9	38.5	28.2	28.8	21.5	10.3
	12	42.3	42.9	37.4	33.5	16.6

$$LaOCl + 2NH_4Cl = LaCl_3 + 2NH_3 + H_2O \quad (7)$$

$$CeO_2 + 2NH_4Cl = CeOCl + 1/2Cl_2 + 2NH_3 + H_2O \quad (8)$$

$$CeOCl + 2NH_4Cl = CeCl_3 + 2NH_3 + H_2O \quad (9)$$

The reactions(6)−(9) illustrate that both La_2O_3 and CeO_2 would be chlorinated below the decomposing temperature of NH_4Cl. All reactions above will be further proved by the thermal decomposition experiments of $LaCl_3 \cdot 7H_2O$ and $CeCl_3 \cdot 7H_2O$.

3.2 Chlorinating mechanism of La_2O_3 and CeO_2

It is clear that the chlorination of La_2O_3 and CeO_2 by NH_4Cl is by no means completed. The chlorinating rate only reaches about 80% even under their optimal condition from the results in Tables 1 and 2. It illustrates that decomposition of $LaCl_3$ and $CeCl_3$ could play an important role in the chlorination on other side. Therefore the investigation of thermal decomposition of $LaCl_3$ and $CeCl_3$ is necessary and useful to understand the mechanism of chlorinating La_2O_3 and CeO_2.

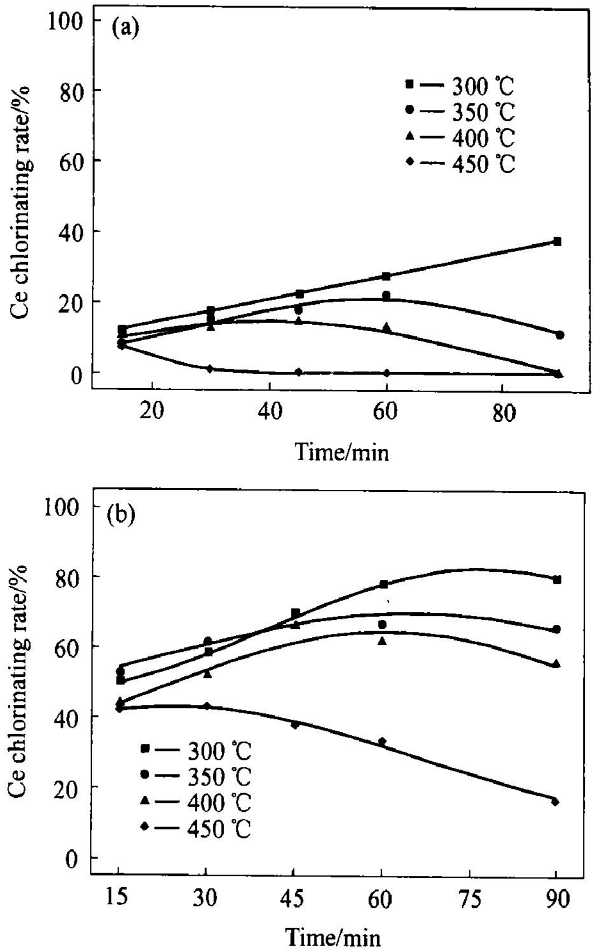

Fig. 1 Ce chlorinating rate at different reaction times
(a) —n = 3; (b) —n = 12

By comparing the results of chlorinating La_2O_3 and CeO_2 by NH_4Cl in Tables 1 and 2, it is found that the chlorination of the CeO_2 and La_2O_3 by NH_4Cl showed the same characteristics. But the CeO_2 consisting of tetravalence cerium is more stable, and it would determine the chlorination of light rare earth such as lanthanum and cerium. Therefore the emphasis of the study should be applied to the thermal decomposition of $CeCl_3 \cdot 7H_2O$.

The $CeCl_3 \cdot 7H_2O$ sample was roasted for 30 min at different temperatures, and the calcine was dissolved into water and filtered. By analysis of trivalence cerium in the filtered solution, the decomposition of $CeCl_3 \cdot 7H_2O$ curve was obtained, as shown in Fig. 2. The result shows that $CeCl_3 \cdot 7H_2O$ is easily oxidized to tetravalence cerium in air and is partially oxidized even at about 100 ℃. Violent oxidization of the $CeCl_3 \cdot 7H_2O$ is observed at temperature near 210 ℃. These findings can be suitable to the hydrolysis of trivalence cerium at the neutral condition[8]:

$$Ce^{3+} + 2H_2O + O_2 \rightleftharpoons Ce(OH)_4 \quad (10)$$

$$Ce(OH)_4 \rightleftharpoons CeO_2 + 2H_2O \quad (11)$$

Obviously the decomposition of $CeCl_3 \cdot 7H_2O$

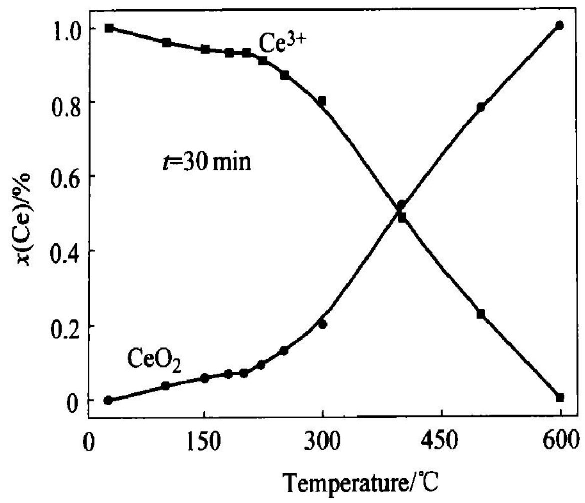

Fig. 2 Thermal decomposition of $CeCl_3 \cdot 7H_2O$ at different temperatures

at higher temperature include three steps: an-hydration, formation of intermediate and further oxidation to CeO_2, which is disclosed to the essence of chlorinating CeO_2. A thermal decomposition experiment of $CeCl_3 \cdot 7H_2O$ is further carried out. The DSC and TGA curves are obtained at a warming-up velocity of 10 ℃/min in air, as shown in Figs. 3 and 4.

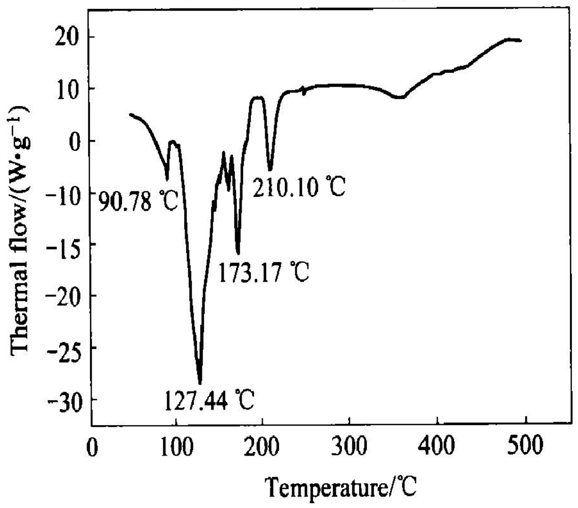

Fig. 3 DSC curve of $CeCl_3 \cdot 7H_2O$

The thermal decomposition and oxidization of $CeCl_3 \cdot 7H_2O$ are multi-step process. It can be seen that there are five obvious endothermic peaks in Fig. 3. The endothermic peak under 100 ℃ is due to removing of the adsorbed water. At the same time, there are five mass loss stages in TGA curve of Fig. 4, which is in according with the endothermic peaks of Fig. 3. The mass loss of the first stage is 1. 207 mg, which equals to the mass loss of four crystal waters for $CeCl_3 \cdot 7H_2O$. The total mass losses of the second, third and fourth stage are 1. 547 mg, 1. 849 mg and 2. 158 mg respectively, which represents the loss of the fifth, sixth and seventh crystal water of $CeCl_3 \cdot 7H_2O$. It should be paid special attention that the mass

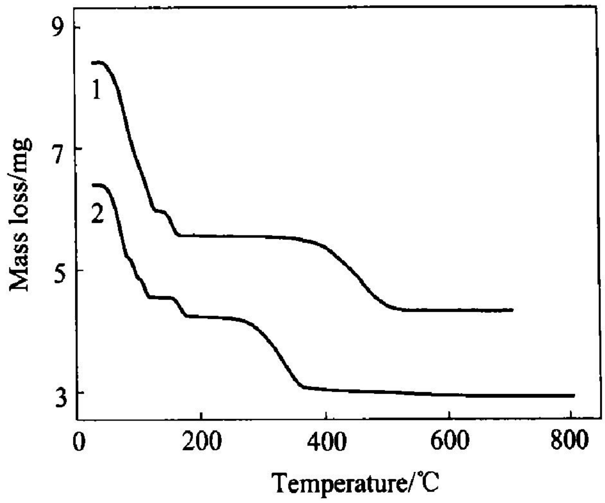

Fig. 4 TGA curves of $LaCl_3 \cdot 7H_2O$ and $CeCl_3 \cdot 7H_2O$

1 — $m(LaCl_3 \cdot 7H_2O)$ = 8. 412 mg;
2 — $m(CeCl_3 \cdot 7H_2O)$ = 6. 393 mg

loss of the fifth stage is 1. 159 mg. If the $CeCl_3$ is oxidized to CeOCl, the mass loss should be 0. 939 mg, and if the $CeCl_3$ is oxidized to CeO_2, the mass loss should be 1. 272 mg. Therefore the fifth stage represents a mixed process, e. g. the products of the thermal decomposition in the stage should be the mixture of CeOCl and CeO_2, and can be represented as follows:

$$CeCl_3 \cdot 7H_2O \longrightarrow CeCl_3 \cdot 3H_2O + 4H_2O \quad (12)$$

$$CeCl_3 \cdot 3H_2O \longrightarrow CeCl_3 \cdot 2H_2O + H_2O \quad (13)$$

$$CeCl_3 \cdot 2H_2O \longrightarrow CeCl_3 \cdot H_2O + H_2O \quad (14)$$

$$CeCl_3 \cdot H_2O \longrightarrow CeCl_3 + H_2O \quad (15)$$

On the other hand, after the $CeCl_3 \cdot 7H_2O$ lose seven crystal waters, the $CeCl_3$ will further be oxidized to CeOCl and CeO_2. Therefore, decomposition of the $CeCl_3 \cdot 7H_2O$ at heating condition is a mixed process of dewatering and oxidizing:

$$CeCl_3 + H_2O = CeOCl + 4HCl \quad (16)$$

$$CeCl_3 + O_2 = CeO_2 + 3/2Cl_2 \quad (17)$$

The same phenomenon is observed for the $LaCl_3 \cdot 7H_2O$ in TGA curve of Fig. 4, but only three stages appears. Their mass losses at each stage are 2. 460 mg, 0. 413 3 mg and 1. 180 mg, respectively. By theoretical calculation, the mass loss of losing six crystal waters for $LaCl_3 \cdot 7H_2O$ should be 2. 446 mg and the mass loss of further losing one water should be 0. 407 7 mg and the mass loss of forming intermediate LaOCl from $LaCl_3$ should be 1. 190 mg. Therefore the thermal decomposition of $LaCl_3 \cdot 7H_2O$ can be represented by the following reactions:

$$LaCl_3 \cdot 7H_2O \longrightarrow LaCl_3 \cdot H_2O + 6H_2O \quad (18)$$

$$LaCl_3 \cdot H_2O \longrightarrow LaCl_3 + H_2O \quad (19)$$

$$LaCl_3 + H_2O = LaOCl + 2HCl \quad (20)$$

The results illustrate that the thermal decomposition of $LaCl_3 \cdot 7H_2O$ and $CeCl_3 \cdot 7H_2O$ could produce the intermediate LaOCl and CeOCl. But the thermal decomposition of $CeCl_3 \cdot 7H_2O$ forms the mixture of CeO_2 and intermediate CeOCl. The chlorination of La_2O_3 and CeO_2 with NH_4Cl can be explained by the formation of intermediates LaOCl and CeOCl, and then further transfers to $LaCl_3$ and $CeCl_3$, respectively. Furthermore $LaCl_3$ and $CeCl_3$ would be oxidized to LaOCl and CeOCl or CeO_2. Therefore in the chlorination of La_2O_3 and CeO_2 by NH_4Cl the reaction temperature and time should be strictly controlled. And it is necessary that over-dosage NH_4Cl should be applied in the chlorination.

4 CONCLUSIONS

1) The chlorinating rate of La_2O_3 and CeO_2 with NH_4Cl can reach about 80% at 300 ℃, and the chlorinating reactions of La_2O_3 and CeO_2 can be represented as follows:

$$La_2O_3 + 2NH_4Cl \longrightarrow 2LaOCl + 2NH_3 + H_2O$$

$$LaOCl + 2NH_4Cl \longrightarrow LaCl_3 + 2NH_3 + H_2O$$

$$CeO_2 + 2NH_4Cl \longrightarrow CeOCl + 1/2Cl_2 + 2NH_3 + H_2O$$

$$CeOCl + 2NH_4Cl \longrightarrow CeCl_3 + 2NH_3 + H_2O$$

2) The thermal analyses of $LaCl_3 \cdot 7H_2O$ and $CeCl_3 \cdot 7H_2O$ illustrate that they start to anhydrate crystal water at about 120 ℃. Six crystal waters anhydrate firstly and successively the seventh crystal water anhydrate for $LaCl_3 \cdot 7H_2O$, and four crystal waters anhydrate and then anhydrate the fifth, sixth and seventh crystal water for $CeCl_3 \cdot 7H_2O$. $LaCl_3$ and $CeCl_3$ are further decomposed to the intermediate LaOCl or CeOCl and CeO_2. The results further prove the existence of LaOCl or CeOCl in the thermal decomposition experiment. Therefore in the chlorination of La_2O_3 and CeO_2 by NH_4Cl the reaction temperature and time should be strictly controlled. Over-dosage NH_4Cl should also be applied in the chlorination.

REFERENCES

[1] XU Guang-xian. Rare Earth[M](Second ed). Beijing: Metallurgical Industry Press, 1995. (in Chinese)

[2] CHI Ru-an, WANG Dian-zuo. Beneficiation of Rare Earth Ore and Extraction Technology[M]. Beijing: Science Press, 1996. 217 - 305. (in Chinese)

[3] ZHU Guo-cai, CHI Ru-an. A recovering method of rare earth carbonate by roasting bastnasite concentrate with NH_4Cl[P]. CN: 99106149.7, 2000.

[4] TIAN Jun, ZHU Guo-cai, CHI Ru-an. Extraction of rare earth with NH_4Cl roasting from bastnasite concentrate[J]. Mining and Metallurgy Engineering, 2000, 20(1): 41 - 43. (in Chinese)

[5] ZHU Guo-cai, TIAN Jun, CHI Ru-an, et al. Recovering RE with NH_4Cl roasting from bastnasite crude ore[J]. The Chinese Journal of Nonferrous Metals, 2000, 10(5): 701 - 704. (in Chinese)

[6] ZHU Guo-cai, CHI Ru-an, TIAN Jun. A novel process of separation of RE and Mn from Panxi rare earth mud[J]. Trans Nonferrous Met Soc China, 2002, 12(1): 164 - 168.

[7] ZHU Guo-cai, CHI Ru-an, XU Sheng-ming. Recovering RE with selective chlorinating from intermediate Baiyunebo concentrate[J]. Chinese Rare Earths, 2002, 23(1): 20 - 26. (in Chinese)

[8] Zhang Q W, Fumio S. Non-thermal process for extracting rare earths from bastnasite by means of mechanochemical treatment [J]. Hydrometallurgy, 1998, 47(2 - 3): 231 - 241.

[9] Metal Department of Zhongshan University(ed). Physicochemistry Constant[M]. Beijing: Metallurgical Industry Press, 1978. (in Chinese)

[10] PAN Ye-jin. The Handbook on Extraction of Nonferrous Metals (Rare Earth Metals)[M]. Beijing: Metallurgical Industry Press, 1993. (in Chinese)

[11] Burns D T, Townshend A, Carter A H. Inorganic Reaction Chemistry (Vol. 2)[M]. New York: John Wiley and Sons, 1981.

(Edited by YANG You-ping)