

Preparation of Cerium-rich Rare Earth Oxide Nanoparticles from Bastnaesite Concentrate

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Abstract. Cerium-rich rare earth oxides nanoparticles were extracted from bastnaesite concentrate by first leaching, alkali fusion with NaOH, and second leaching process. The effects of the hydrochloric acid concentration, mass ratio of solid to liquid, leaching temperature of the leaching process, and the NaOH amount, roasting temperature and roasting time of alkali fusion process were systematically studied by X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD) and transmission electron microscope (TEM) analysis. The optimum parameters of the leaching process were 2 mol·L⁻¹ HCl solution, solid to liquid mass ratio 1: 5 and 75 °C, respectively. Non-rare earth impurities could be effectively removed by roasting the first sludge with 30wt. % NaOH. The grade of total rare earth oxides and the purity of CeO₂ in the final product were 96.99% and 78.73%, respectively, which were improved by 10.62% and 5.73% than that of one step leaching. The cerium-rich rare earth oxides powder showed a major phase of ceria, with particle size distribution of 20~100nm according to TEM.

1. Introduction

Cerium oxide is a rare earth oxide with special physical and chemical properties. At present it has been widely used in chemical machine polishing (CMP), catalysts, ultraviolet blocker, optical devices, ceramic, fuel cells and so on. Because of its excellent cutting ability, short polishing time, high polishing precision, clean operating environment, and better effect compared with the other polishing powders [1, 2], cerium oxide is especially considered candidate in the field of CMP.

Usually cerium oxide is prepared by two ways: liquid phase method and extracting from bastnaesite. The advantage of liquid method is obvious, small particle size and high purity cerium oxide can be easily obtained under ambient condition with cerium salts, such as sol-gel method, hydrothermal method and micro-emulsion method. However, the grain coarsening and aggregation in liquid phase usually lead to inhomogeneous powders, and expensive raw material and sophisticated production equipment make the industrialization difficult [3, 4].

The other important way to obtain cerium oxide is directly extracted from the bastnaesite. As a main industrial mineral, bastnaesite is the largest proven reserve among all rare earth (RE) minerals in the world [5]. For example, rich resources of bastnaesite were found in Mianning, Sichuan and Huishan, Shandong in China [6-8]. Zhou Jing et al. [9] roasted bastnaesite with auxiliary agent, and leached the cerium with sulfuric acid after washing the calcine with water. The cerium (IV) and other RE elements were separated by P204 extraction, and cerium product was obtained by washing and reverse extraction. Liu Zhaogan et al. [10] roasted the bastnaesite with sodium carbonate and washed out NaF with water. The cerium (IV) was separated from other RE elements by leaching with dilute hydrochloric acid, and the sludge was the Ce rich concentrate. R. CHI et al. [11] leached the sludge with concentrated hydrochloric acid and hydrogen peroxide, high-purity cerium (IV) oxide was recovered from the leachate by precipitation using oxalic acid and roasting, in which $\text{CeO}_2/\sum \text{REO} > 95\%$, and the recovery of cerium is 85.3%.

Hui Zhong[12] put forward a new roasting decomposition method of bastnaesite in NaHCO_3 . After washing the NaF using water, the sludge was leached with dilute hydrochloric acid ($3\text{mol}\cdot\text{L}^{-1}$) to separate cerium oxide from trivalent RE elements, calcium and iron etc. The purity of cerium oxide reached 72% in the product by this method, however, the factors in leaching process were not optimized. In this paper, we improved Zhong's method. The sludge of first leaching was roasted with NaOH, then the calcinate was leached again to enhance the purity of cerium oxide and the grade of rare earth in the product, and the factors in the first leaching process were studied in detail.

2. Experimental

2.1. Materials

The bastnasite concentrate in the experiment was from Dechang, located in the Sichuan province in China. The mineral material was crushed and sieved to 0.075mm , and main compositions were shown in the Table 1. The total rare earth oxide was 57.43 wt. %, and CeO_2 was 30.29 wt. %.

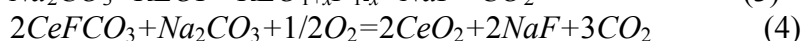
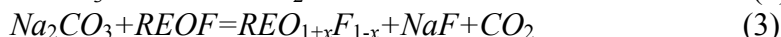
Table 1. Main Chemical Compositions of Bastnaesite Concentrate (wt.%).

| | | | | | | |
|--------------|----------------|-------------------------|-------------------------|-------------------------|--------------|----------------|
| Compositions | CeO_2 | La_2O_3 | Nd_2O_3 | Fe_2O_3 | CaO | SiO_2 |
| Percentage | 30.29 | 20.68 | 6.46 | 6.53 | 7.71 | 5.66 |
| Compositions | SrO | Al_2O_3 | SO_3 | BaO | F | Others |
| Percentage | 4.13 | 2.06 | 4.80 | 1.90 | 8.29 | 1.49 |

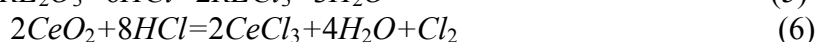
2.2. Methods

20 g bastnasite concentrate was mixed well with 4g NaHCO_3 , and roasted at 600°C for two hours. The calcinate was washed with water to remove Na_2CO_3 , NaF etc, then leached with concentrated hydrochloric acid. The sludge was roasted with NaOH in a muffle furnace, and washed with dilute HCl for second time. Finally rare earth oxide rich in cerium was obtained by roasting the second sludge.

The reactions during the roasting decomposition in NaHCO_3 were shown as formula 1-4.



The main reactions in the first leaching process were shown as formula 5, 6. $\text{RE}_2\text{O}_3 + 6\text{HCl} = 2\text{RECl}_3 + 3\text{H}_2\text{O}$ (5)



2.3. Analysis

X-ray diffraction (XRD) analysis of the samples were performed on a X-ray diffractometer (Fang Yuan, DX-2700) with $\text{CuK}\alpha$ radiation (30 mA, 40 kV, $\lambda = 0.154184\text{nm}$) in the 2θ range from 20° to 72° . The compositions of the sludges were determined by X-ray fluorescence spectrometry (XRF, Shiadzu, XRF-1800) with a rhodium tube as the source of radiation (4kW, 85mA). The morphology and size of product were characterized by transmission electron microscope (TEM, Carl Zeiss Libra 200FE).

The grade of total rare earth oxides and the purity of cerium oxide in the sludge were expressed by $\sum\text{REO}$ and $w_1(\text{CeO}_2)$, respectively, as shown in formula 7 and 8. The grade of cerium oxide was expressed by $\text{CeO}_2/\sum\text{REO}$, which was calculated based on the grade of total rare earth oxides in the sludge (formula 9). The recovery of cerium was expressed by the formula 10, in which m_0 and w_0 were the mass and cerium purity of the bastnasite concentrate, m_1 and w_1 were the mass and cerium purity of the sludge, respectively.

$$\sum\text{REO} = \frac{m(\text{REO})}{m(\text{sludge})} \times 100\% \quad (7)$$

$$w_1(\text{CeO}_2) = \frac{m(\text{CeO}_2)}{m(\text{sludge})} \times 100\% \quad (8)$$

$$\text{CeO}_2/\sum\text{REO} = \frac{m(\text{CeO}_2)}{m(\text{REO})} \times 100\% \quad (9)$$

$$x(Ce) = \frac{m_1 w_1}{m_0 w_0} \times 100\% \quad (10)$$

3. Results and discussion

3.1. Factors in leaching

After being roasted with NaHCO_3 and washed with water, the calcinate was leached with concentrated hydrochloric acid to dissolve impurities and improve the purity of product. The effects of the hydrochloric acid concentration, the mass ratio of solid to liquid and the leaching temperature on the grade of cerium oxide ($\text{CeO}_2/\sum\text{REO}$) and total rare earth oxides ($\sum\text{REO}$) were studied.

3.1.1. The hydrochloric acid concentration

The effect of HCl concentration on the grade of cerium oxide ($\text{CeO}_2/\sum\text{REO}$) and the grade of total rare earth oxides ($\sum\text{REO}$) were shown in Fig.1. With HCl concentration increasing, $\text{CeO}_2/\sum\text{REO}$ increased from 69.84 wt.% to 93.46 wt.%, which was due to the trivalent rare earths dissolved in HCl solution in the form of RECl_3 (equation 5), and most CeO_2 remained in the leach sludge. For the dilute HCl solution ($<2\text{mol}\cdot\text{L}^{-1}$), the $\sum\text{REO}$ in the sludge remained about 82 wt. %. However, when the HCl concentration was higher than $2\text{mol}\cdot\text{L}^{-1}$, $\sum\text{REO}$ reduced obviously. For $3\text{mol}\cdot\text{L}^{-1}$ HCl solution, $\sum\text{REO}$ was only 64.31 wt%. CeO_2 as well as other rare earth oxides reacted with high concentration HCl solution, and dissolved in the form of CeCl_3 (equation 6) [11], which resulted the loss of cerium and decrease of $\sum\text{REO}$ in the sludge. The optimal concentration of hydrochloric acid in the first leaching was chosen $2\text{mol}\cdot\text{L}^{-1}$, considering the grade of cerium oxide and the grade of total rare earth oxides.

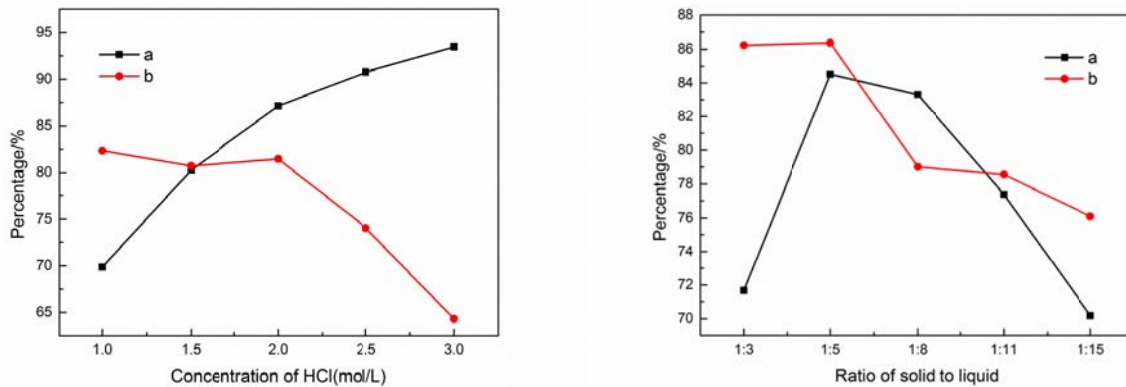


Fig.1. Effect of the hydrochloric acid concentration on (a) $\text{CeO}_2/\sum\text{REO}$ and (b) $\sum\text{REO}$ (45°C, 1h, mass ratio of solid to liquid 1:5). **Fig.2.** Effect of the mass ratio of solid to liquid on (a) $\text{CeO}_2/\sum\text{REO}$ and (b) $\sum\text{REO}$ (75 °C, 1h, ratio of solid to liquid 1:5). $2\text{mol}\cdot\text{L}^{-1}$ HCl).

3.1.2. Mass ratio of solid to liquid

Besides concentration, the amount of HCl solution was also taken into consideration. The effect of the mass ratio of solid to liquid on $\text{CeO}_2/\sum\text{REO}$ and $\sum\text{REO}$ were shown in Fig.2. $\sum\text{REO}$ decreases gradually with the decreasing of solid to liquid from 1:3 to 1:15, which was due to more rare earths elements dissolving into hydrochloric acid solution. However, $\text{CeO}_2/\sum\text{REO}$ first increases and then decreases, which reaches the largest grade at the mass ratio 1:5. Based on the rare earth oxides of bastnasite concentrate, hydrochloric acid dosage was not enough to dissolve all the rare earths at mass ratio 1:3, so trivalent non-Ce rare earths were mainly leached (reaction 5) and most of Ce remained as CeO_2 in the sludge. However, with more HCl solution used, CeO_2 reacted with the high dosage hydrochloric acid and formed CeCl_3 dissolving in the solution, leading to the decrease of $\text{CeO}_2/\sum\text{REO}$ in the sludge. Thus, the optimal ratio of solid to liquid was 1:5.

3.1.3. Leaching temperature

The effect of leaching temperature on $\text{CeO}_2/\sum\text{REO}$ and $\sum\text{REO}$ were shown in Fig.3. When leaching solution was heated, $\sum\text{REO}$ in the sludge first rose and then decreased, and reached the maximum at 75 °C. The reason was the non-rare earth impurities reacted with hydrochloric acid significantly with the temperature rising, which was leached in the solution. However, the

volatilization of hydrochloric acid gas became more and more obvious when the reacting temperature above 75°C. $\text{CeO}_2/\Sigma\text{REO}$ presented a downward trend with the increasing temperature, because more cerium dissolved in solution in the form of CeCl_3 with the oxidation ability of CeO_2 increased as the temperature rising, resulting in $\text{CeO}_2/\Sigma\text{REO}$ gradually decreases. Therefore, 75 °C was chosen as the optimum temperature in the leaching process.

In conclusion, in the first leaching process, hydrochloric acid concentration and the mass ratio of solid to liquid showed significant influence on $\text{CeO}_2/\Sigma\text{REO}$ and ΣREO than temperature. Under the optimal conditions, ΣREO and $\text{CeO}_2/\Sigma\text{REO}$ could reach 86.37wt% and 84.52wt%, respectively, while the recovery of cerium was 84.03%, which was obviously enhanced than Zhong's work[12].

3.2. Alkali fusion

The sludge of first leaching was roasted with NaOH, and then experienced second hydrochloric acid leaching to further purify. In the process of alkali fusion, the NaOH amount, roasting temperature and roasting time were studied, and the NaOH amount was the key factor according to the study.

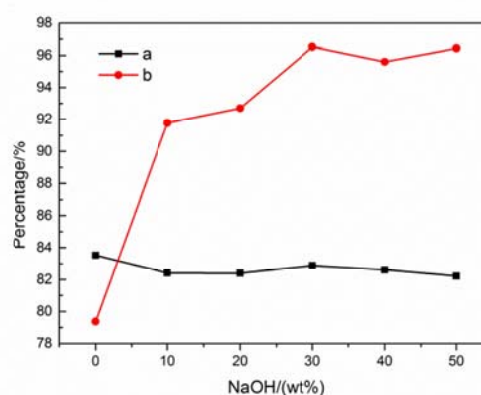
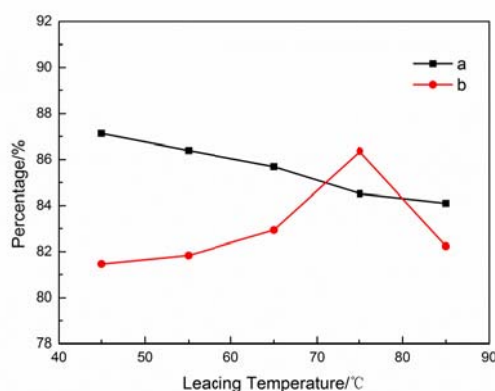


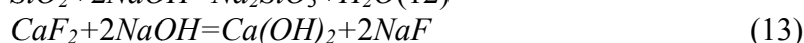
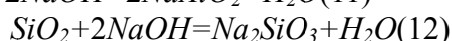
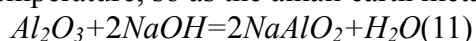
Fig.3. Effect of leaching temperature on (a) $\text{CeO}_2/\Sigma\text{REO}$ and (b) ΣREO (2 mol·L⁻¹ HCl, 1h, ratio of solid to liquid and (b) ΣREO (600 °C, 1h).
Fig.4. Effect of NaOH on (a) $\text{CeO}_2/\Sigma\text{REO}$ and (b) ΣREO (600 °C, 1h).
1:5).

3.2.1. Effect of NaOH amount

The effect of the NaOH amount on the grade of cerium oxide ($\text{CeO}_2/\Sigma\text{REO}$) and total rare earth oxides (ΣREO) were shown in Fig.4. The addition of 10wt. % NaOH into first sludge resulted in an increase of ΣREO , 91.77% compared with 79.37% of first sludge. This demonstrated the process of alkali fusion efficiently reduced the non-rare earth impurities, which was due to the reaction between the non-rare earth impurities and NaOH.

ΣREO in sludge enhanced with the NaOH amount increasing, and reached the maximum of 96.53wt. % at 30wt. % addition. More NaOH amount was not necessary for no obvious increase of ΣREO . $\text{CeO}_2/\Sigma\text{REO}$ was almost unchanged with the variation of the NaOH amount. Thus, the optimal NaOH amount was 30%.

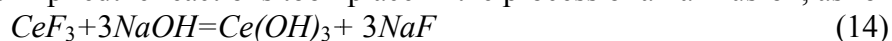
The content of the main chemical compositions of sludges before and after alkali fusion treatment with 30 wt. % NaOH addition was shown in table 2. The content of rare earth oxides CeO_2 , La_2O_3 and Nd_2O_3 increased significantly compared with that of before, while non-rare earth impurities such as oxides of Fe, Si, Ca and Sr etc. decreased obviously, which indicated the non-rare earth impurities reacted with NaOH and were removed by washing, resulting in the remarkable increase of ΣREO . Aluminosilicate, as the common impurities in bastnaesite, could react with NaOH to form water soluble salts, as shown formula 11 and 12. According to the report of literature [13], fluorite (CaF_2) could also react with NaOH to form Ca(OH)_2 (formula 13), when calcinated at high temperature, so as the alkali earth metal Ba.



Therefore, the fluorite, the oxides, and the sulfates which remained in the first sludge could be

leached in the second leaching after alkali fusion, and the ΣREO enhanced.

The XRD patterns of sludge before and after alkali fusion were shown in Fig.5. The major phases before alkali fusion were CeO_2 and CeF_3 , however, NaF appeared and CeF_3 disappeared after alkali fusion. This implied the reactions took place in the process of alkali fusion, as formula 14, 15.



In conclusion, alkali fusion significantly reduced the non-rare earth impurities, thereby ΣREO and $\text{CeO}_2/\Sigma\text{REO}$ were both enhanced.

Table 2. Main Chemical Compositions of Sludge before and after Alkali Fusion (wt.%).

| Compositions | CeO ₂ | La ₂ O ₃ | Nd ₂ O ₃ | Fe ₂ O ₃ | SiO ₂ | CaO | SrO | Al ₂ O ₃ | SO ₃ | BaO |
|----------------------|------------------|--------------------------------|--------------------------------|--------------------------------|------------------|------|------|--------------------------------|-----------------|------|
| Before alkali fusion | 68.13 | 8.72 | 2.02 | 4.4 | 3.96 | 1.84 | 2.15 | 0.82 | 2.19 | 1.29 |
| After alkali fusion | 80.01 | 13.98 | 2.55 | 0.35 | 0.25 | 0.51 | 0.60 | 0.10 | 0.33 | 0.33 |

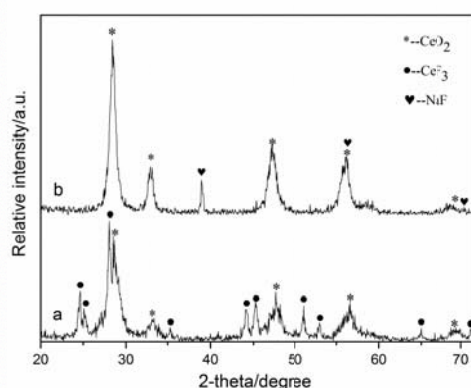


Fig.5. XRD patterns of sludge before Alkali Fusion (a)

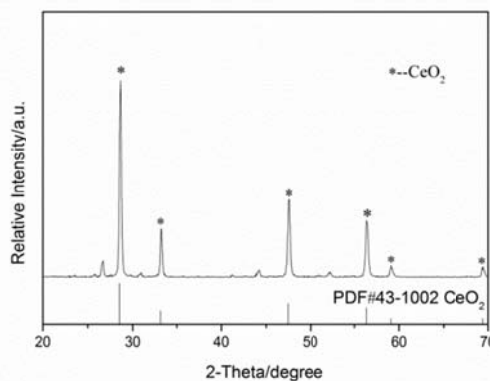


Fig.6. XRD pattern of Ce-rich rare earth oxides and after Alkali Fusion (b). nanoparticles.

3.2.2. Result of alkali fusion

To verify the effect of the alkali fusion, $\text{CeO}_2/\Sigma\text{REO}$, ΣREO , the recovery of cerium ($x(\text{Ce})$) and the purity of CeO_2 ($w_1(\text{CeO}_2)$) in the first and second sludge were summarized in table 3, which sludge were obtained as the optimal conditions described above. The purity of CeO_2 ($w_1(\text{CeO}_2)$) and the grade of total rare earth oxides (ΣREO) after alkali fusion treatment were enhanced 5.73wt.% and 10.62wt.%, respectively, while the recovery of cerium ($x(\text{Ce})$) and $\text{CeO}_2/\Sigma\text{REO}$ showed a little decrease comparing with that of first sludge. The main reason of the decrease in $\text{CeO}_2/\Sigma\text{REO}$ was the increase of ΣREO . The reason of the decrease in cerium recovery was the loss in the process of alkali fusion and second leaching, however, the loss was acceptable considering the remarkable improve of purity. So, the alkali fusion and second acid leaching process was proven to be effective and necessary.

Table3.Comparison of Sludge of first and second time (wt. %).

| | $\text{CeO}_2/\Sigma\text{REO}$ | ΣREO | $x(\text{Ce})$ | $w_1(\text{CeO}_2)$ |
|-----------------------|---------------------------------|--------------------|----------------|---------------------|
| Sludge of first time | 84.52 | 86.37 | 84.03 | 73.00 |
| Sludge of second time | 81.17 | 96.99 | 82.89 | 78.73 |

3.3. Characterization of product

Cerium-rich rare earth oxides product was obtained by calcining the second sludge. The XRD pattern of the product was shown in Fig.6. The main diffraction peaks located at $2\theta=28.55^\circ$, 33.08° , 47.48° , 56.34° , 59.09° and 69.42° were in good agreement with the crystal face (111), (200), (220), (311), (222) and (4 0 0) of ceria, respectively, which indicated the major phase in the product was ceria. The particle size of the product calculated by Scherer formula was about 32 nm. Fig.7 shows the TEM micrograph of the product. The powders obtained were regular in equiaxed geometric contour, which particle size distribution was 20~100nm. The surface quality of polished material was significantly influenced by the contour of ceria polishing powder. As most particles of the product showed obtuse angles, high surface quality was believed to be obtained[14].

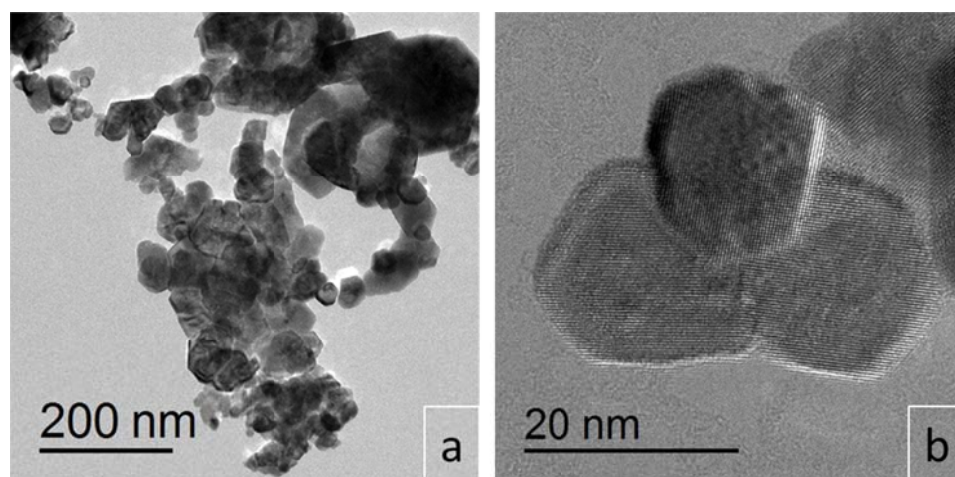


Fig.7.TEM micrographs of Ce-rich rare earth oxides nanoparticles.

4. Conclusion

In this paper, bastnasite was roasted with NaHCO_3 , washed with water and then taken as the material. Ce-rich rare earth oxide nanoparticles powder was obtained by first leaching, alkali fusion with NaOH , and second leaching process.

In the first leaching process, hydrochloric acid concentration and the mass ratio of solid to liquid showed significant influence on $\text{CeO}_2/\Sigma\text{REO}$ and ΣREO than leaching temperature. The optimal leaching conditions were $2\text{mol}\cdot\text{L}^{-1}\text{HCl}$, solid to liquid mass ratio 1:5 and 75°C , respectively. In the process of alkali fusion, NaOH amount exhibited more effect on $\text{CeO}_2/\Sigma\text{REO}$ and ΣREO than roasting temperature and roasting time.

The non-rare earth impurities such as oxides of Fe, Si, Ca and Sr etc. were removed in the alkali fusion with NaOH and second leaching treatment, resulting in the remarkable improvement of ΣREO and the purity of CeO_2 in the product. ΣREO was as high as 96.99%, comparing 86.37% in the first sludge. The purity of CeO_2 was 78.73%, 5.73wt% higher than that of the first sludge. The product obtained by this method may be used as high quality polishing powder.

Acknowledgments

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