

Study on Extraction of Ceric Oxide from Monazite Concentrate

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Abstract - Cerium oxide is to be recovered from monazite, which contains about 27.35% CeO₂. The principal objective of this study is to be able to extract cerium oxide from monazite of Moemeik Myitsone Area. The treatment of monazite in this study involves three main steps; extraction of cerium hydroxide from monazite, solvent extraction of cerium hydroxide, and precipitation with oxalic acid and calcination of cerium oxalate.

Keywords – Calcination, Digestion, Precipitation, Solvent Extraction

I. INTRODUCTION

Cerium is the most abundant of the metals of the so-called rare-earths. It is found in a number of minerals including monazite, bastnasite, gadolinite, fergusonite, samarskite, xenotime, ytrocercite, cerite and allanite (also known as orthite), etc. Monazite and bastnasite are presently the two more important sources of cerium [1].

In Myanmar, Cerium can be extracted from monazite and is discovered locally as heavy sands in Myitsone area, Moemeik Township, Homelain area, Sagaing Division, Thabeikyin Township and Kanbauk and Heinze area, Tanintharyi Division. Rare Earth elements are found in combination with mineral deposits widespread throughout the world. They have very similar physical and chemical properties. Therefore their separation processes are extremely difficult [2].

Cerium is a component of misch metal, which is extensively used in the manufacture of pyrophoric alloys for cigarette lighters, making aluminium alloys and in some steels and irons. In cast iron it opposes graphitization and produce malleable iron, in stainless steel it is used as a precipitation hardening agent. It is also used as a glass polishing agent in glass industry. The oxide is an important constituent of incandescent gas mantles and is emerging as a hydrocarbon catalyst in "self cleaning" ovens. In this application, it can be incorporated into oven walls to prevent the collection of cooking residues [1].

II. EXPERIMENTAL PROCEDURE

Monazite from Moemeik Myitsone Area was used as raw material for the experiments. Monazite was ground to obtain -325 mesh. It has beach color. Flow diagram of the extraction of ceric oxide from monazite concentrate is shown in figure (1).

Caustic Soda Digestion

Required amount of commercial caustic soda and distilled water were put into the conical flask and heated on a sand bed.

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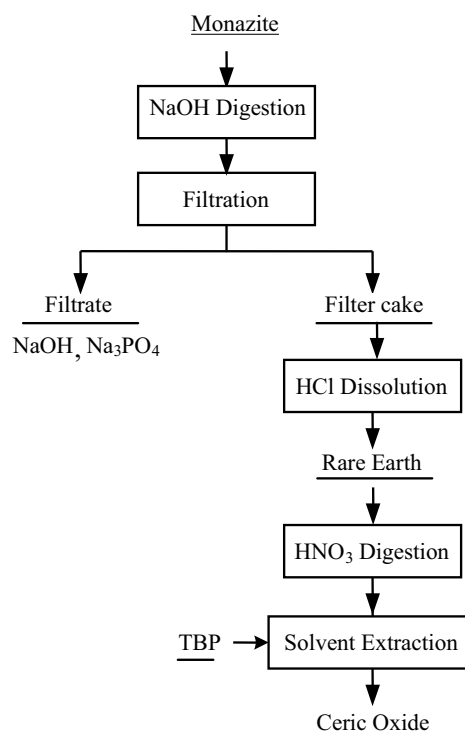
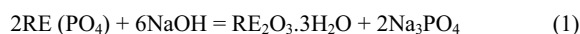


Figure (1) Flow Diagram of the Extraction of Ceric Oxide from Monazite Concentrate

When caustic soda had dissolved, 50 gm of -325 mesh monazite was slowly added to the solution [2]. The reaction of monazite and caustic soda is shown by equation (1) [3].



The mixture was often shaken by hand and heated to 140°C. Leaching time was three hours at this temperature. Leaching temperature was controlled by adding small amount of distilled water into the mixture.

After three hours, the mixture was diluted with distilled water at 105°C for one hour. In the resultant hot slurry, all the original phosphorus was present in solution as trisodium phosphate, and other associated minerals and rare earths were present as a hydrous metal oxide cake. And then this slurry was filtered. The filtration was carried out at 80°C to keep caustic soda and trisodium phosphate in solution. The metal oxide cake was washed with hot water until all the trisodium phosphate and free caustic soda had been removed from the cake. This cake has beach color [3].

Hydrochloric Acid Dissolution

Hydrous metal oxide cake was dried in the drying oven at 100°C for one hour. Then the dried cake was put into conical flask and dissolved in 37% hydrochloric acid at 79°C for one hour. The reaction is presented in equation (2) [3]. And then, this solution was diluted with hot water for one hour. Other

associated minerals and rare earths dissolved in acid solution and undissolved impurities were left as residue. This solution changes to yellow color. This process is shown in figure (2).

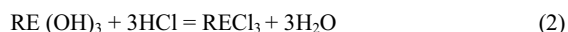


Figure (2) Hydrochloric Acid Dissolution

Selective Precipitation

The acid solution (filtrate from Hydrochloric Acid dissolution) was precipitated with ammonium hydroxide. Other associated minerals hydroxide was precipitated at pH-5.8 and rare earth hydroxide was precipitated at pH-11. The rare earth hydroxide was dried in the drying oven at 100°C for one hour [3], [4]. Precipitation of yellow color rare earth hydroxide is shown in figure (3).



Figure (3) Precipitation of rare earth hydroxide

Digestion of Rare Earth with Nitric Acid

50 gm of rare earth hydroxide was slowly added to 50% nitric acid solution. The ratio of rare earth hydroxide and acid solution was 1:2. This mixture was heated at 90°C until complete dissolution for about one hour. The acid solution was cooled by air and treated to 300 ml solution by adding distilled water.

This solution was precipitated at pH-3.8 by adding ammonium hydroxide. Then filtration was made. After filtration, the residue (cerium hydroxide) and the filtrate (other rare earths) were obtained. This residue is dried in an oven at 100°C for one hour.

The filtrate (other rare earths) was precipitated at pH-11 by adding ammonium hydroxide. After filtration, the residue was dried in an oven at 100- 200°C for 1- 2 hours [4]. Cerium hydroxide has yellow color.

Solvent Extraction of Cerium Hydroxide

The objective of solvent extraction is to obtain high purity cerium hydroxide.

Preparation of Aqueous Solution

7 N nitric acid solution was put into a beaker and 10 gm of cerium hydroxide was slowly added to acid solution. When the reaction is complete, aqueous solution was prepared to get a total volume of 200 ml. This solution changes to red color. Preparation of aqueous solution is shown in figure (4).



Figure (4) Preparation of aqueous solution

Extraction

100 ml aqueous solution and 100 ml of tributyl-phosphate (TBP) were put into the separatory funnel. This solution was shaken with shaker for five minutes. Organic rich solution and raffinate were obtained. Cerium hydroxide and small amount of impurities were dissolved in the solvent. Other impurities and very small amount of cerium hydroxide remained in the raffinate [5]. Extraction of cerium hydroxide with TBP is shown in figure (5).



Figure (5) Extraction with TBP

Stripping

The organic rich solution was stripped with 3% hydrogen peroxide for five minutes as shown in figure. The ratio of organic solution to hydrogen peroxide was 1:1. Stripping was done twice. Organic solution and pregnant solution were obtained [5]. The pregnant solution changes to white color. The stripping step is shown in figure (6).



Figure (6) Stripping with hydrogen peroxide

Precipitation

Pregnant solution was put in a beaker and heated to boil to evaporate hydrogen peroxide. By adding ammonium hydroxide or 10% oxalic acid to the pregnant solution,

cerium hydroxide or cerium oxalate was precipitated as shown in figure (7) and then filtered. The precipitate was washed with hot water until pH is 7. And this precipitate was dried in an oven at 100°C for 1 hour and calcined at 1000°C for 1 hour. After calcination, cerium oxide changes to pink color from yellow color.



Figure (7) Precipitation of Cerium Hydroxide after solvent extraction process

III. RESULTS AND DISCUSSION

Monazite from Moemeik Myitsone Area is analyzed by X-Ray Fluorescence Spectrometer (XRF) and its first stage of flow diagram is shown in table (1).

Table (1) Analysis of Monazite from Moemeik Myitsone Area

| No | Element | XRF analysis (%) |
|----|---|------------------|
| 1 | P ₂ O ₅ | 26.73 |
| 2 | SiO ₂ | 4.3 |
| 3 | ZrO ₂ | 1.36 |
| 4 | TiO ₂ | 2.75 |
| 5 | Fe ₂ O ₃ | 1.15 |
| 6 | CeO ₂ | 27.35 |
| 7 | La ₂ O ₃ | 13.44 |
| 8 | Y ₂ O ₃ | 1.71 |
| 9 | Nd ₂ O ₃ | 3.34 |
| 10 | Pr ₆ O ₁₁ | 1.65 |
| 11 | Other rare earths & associated minerals | 16.22 |

Rare Earths oxide is analyzed by X-Ray Fluorescence Spectrometer (XRF) and its six stage of flow diagram is shown in table (2).

Table (2) Analysis of Rare Earths Oxide

| No | Element | XRF analysis (%) |
|----|---------------------------------|------------------|
| 1 | CeO ₂ | 31.74 |
| 2 | La ₂ O ₃ | 23.05 |
| 3 | Y ₂ O ₃ | 6.56 |
| 4 | Nd ₂ O ₃ | 20.37 |
| 5 | Pr ₆ O ₁₁ | 6.59 |
| 6 | Sm ₂ O ₃ | 6.95 |
| 7 | Gd ₂ O ₃ | 4.74 |

Ceric oxide is analyzed by X-Ray Fluorescence Spectrometer (XRF) and its last stage of flow diagram is shown in table (3).

Table (3) Analysis of Ceric Oxide

| No | Element | XRF analysis (%) |
|----|--------------------------------|------------------|
| 1 | CeO ₂ | 96.03 |
| 2 | Nd ₂ O ₃ | 1.01 |
| 3 | La ₂ O ₃ | 1.09 |
| 4 | Other rare earths | 1.87 |

Digestion Process

There are four types of digestion process. They are

- (1) Caustic Soda Digestion
- (2) Sulfuric Acid Digestion
- (3) Perchloric Acid Treatment
- (4) Nitric Acid Treatment

Caustic soda digestion process is widely used in the world, as it is more economic and easy to handle. So caustic soda digestion was chosen in this paper. In caustic soda digestion, sand to caustic ratios of 1:2, 1:2.5, 1:2.75, 1:3, 1:3.5 and 1:4 were investigated at 140°C for 3 hrs. Among them, 1: 2.75 is the best. In this ratio, the weight of the residue is decreased.

Precipitation after Solvent Extraction Process

Pregnant solution obtained from solvent extraction process was precipitated with ammonium hydroxide and oxalic acid. The result of precipitate with oxalic acid was better than that of ammonium hydroxide. X-Ray Fluorescence Spectrometer (XRF) result of cerium oxide by oxalic precipitation was 96.03% and XRF result of cerium oxide by ammonium hydroxide precipitation was 80%.

IV. CONCLUSION

Cerium is recovered from Moemeik Myitsone Monazite which contains about 27.35% CeO₂. The particle size (-325 mesh size monazite) was digested with caustic soda. In caustic soda digestion process, monazite to caustic ratio of 1: 2.75, digestion time of 3hrs and temperature of 140°C were obtained as the optimum condition. In hydrochloric acid dissolution, 1.5 kg acid per kg monazite, dissolution time 1 hr and temperature 79°C were tested. In nitric acid digestion process, digestion time 1 hr and temperature 90°C were tested.

In solvent extraction process, tributylphosphate (TBP) was used as solvent. Stripping was done for two times. After solvent extraction process, pregnant solution was precipitated with oxalic acid and calcined of cerium oxalate to cerium oxide at 1000°C for 1 hour and got 96.03% cerium oxide.

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