

Study on Extraction of Lanthanum Oxide from Monazite Concentrate

Nwe Nwe Soe, Lwin Thuzar Shwe, and Kay Thi Lwin

Abstract—Lanthanum oxide is to be recovered from monazite, which contains about 13.44% lanthanum oxide. The principal objective of this study is to be able to extract lanthanum oxide from monazite of Moemeik Myitsone Area. The treatment of monazite in this study involves three main steps; extraction of lanthanum hydroxide from monazite by using caustic soda, digestion with nitric acid and precipitation with ammonium hydroxide and calcination of lanthanum oxalate to lanthanum oxide.

Keywords—Calcination, Digestion, Precipitation.

I. INTRODUCTION

LANTHANUM was discovered in 1839 by Swedish Chemist Carl Gustav Mosander when he partially decomposed a sample of cerium nitrate by heating and treating the resulting salt with nitric acid. From the resulting solution, new rare earth, lanthanum was isolated in relatively pure form in 1923.

Lanthanum can also be classified as a rare earth element. The rare earth elements are the 15 elements that make up row 6 of the periodic table. That group of elements is also called the lanthanides. Lanthanum is relatively common in the Earth's crust. Its abundance is thought to be as high as 18 parts per million. That would make it nearly as common as copper or zinc. Unlike those metals, however, it usually does not occur in one place, as in copper mines. Instead, it is spread widely throughout the Earth's crust. It is found in a number of minerals including monazite, bastnasite, gadolinite, fergusonite, samarskite, xenotime, yttracrite, cerite and allanite (also known as orthite), etc. Its most common minerals are monazite, bastnasite [1].

In Myanmar, Lanthanum 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].

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La_2O_3 has more extensive applications. It is a white amorphous powder; insoluble in water improves the alkali resistance of glass. The Kodak's camera objectives contain from 20 to 40% La_2O_3 . Lanthanum oxide can also be used in optical glasses where it imparts improved alkali resistance, La-Ce-Tb phosphors for fluorescent lamps, dielectric and conductive ceramics, Barium titanate capacitors, X-Ray intensifying screens and lanthanum metal production [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. The flow diagram of the extraction of lanthanum oxide is shown in Fig. 1.

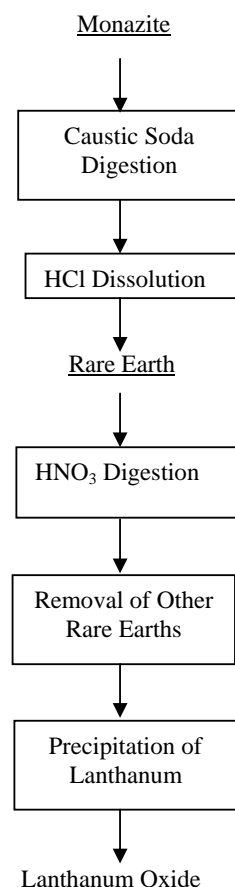
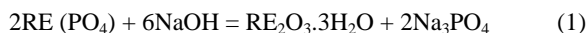


Fig. 1 Flow Diagram of Extraction of Lanthanum Oxide

Caustic Soda Digestion

Required amount of commercial caustic soda and distilled water were put into the conical flask and heated on a sand bed. When caustic soda had dissolved, (-325) mesh monazite was slowly added to the solution. The reaction of monazite and caustic soda is shown in 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 rare earths and other associated minerals 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.

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. After HCl dissolution, the color changes from beach color to yellow. This process, third stage of the flow diagram, is shown in Fig. 2.



Fig. 2 HCl Dissolution of Hydrous Metal Oxide Cake

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. After that, it has yellow color. Precipitation of rare earth hydroxide, fourth stage of flow diagram, is shown in Fig. 3.



Fig. 3 Precipitation of Rare Earth Hydroxide

Digestion of Rare Earth with Nitric Acid

Rare earth hydroxide was digested with nitric acid solution. This mixture was heated at 90°C until complete dissolution for about one hour. The rare earth solution was oxidized with potassium permanganate and precipitated with sodium carbonate at pH-3.8. Then cerium carbonate was obtained. After filtration, the solution was precipitated with oxalic acid and calcined at 1000°C, and then the rare earth oxide without cerium was obtained. After cerium removing, the color changes from yellow to pale yellow.

Precipitation of pH values for Rare Earth Hydroxide

TABLE I
PRECIPITATION OF PH VALUES FOR RARE EARTH HYDROXIDE

Rare Earth	Nitrate Solution		Solubility g-mol/L $\times 10^6$
	pH at precipitation	pH at $\text{OH}^-/\text{R}^{+++}=0.1$	
Scandium	~6.3		~0.05
Yttrium	6.83	6.90	1.2
Lanthanum	7.82	8.23	7.8
Cerium	7.60	7.76	4.8
Praseodymium	7.35	7.67	5.4
Neodymium	7.31	7.40	2.7
Samarium	6.92	7.08	2.0
Europium	6.82	6.90	1.4
Gadolinium	6.83	6.94	1.4
Erbium	6.76	6.84	0.8
Thulium	6.40	6.70	0.6
Ytterbium	6.30	6.65	0.5
Lutetium	6.30	6.63	0.5

Rare earth metals have similar physical and chemical properties. Therefore their separation processes are extremely difficult. But they can be separated by selective precipitation process. So firstly, the rare earth hydroxide after cerium removal was digested with nitric acid. According to the Table I [2], medium rare earths and heavy rare earths start to precipitate from pH-6.3 to pH-6.92 and lanthanum start to precipitate at pH-7.82 in nitric media. In order to get lanthanum, medium, heavy and other rare earths were needed to remove by selective precipitation method.

Removal of Medium Rare Earths and Heavy Rare Earths

To remove medium rare earths and heavy rare earths, the rare earth oxides after cerium removal was digested with nitric acid and diluted with water. The digestion of rare earth oxide with nitric acid, stage five of the flow diagram, is shown in Fig. 4. At this stage the color is red brown. Then the solution was precipitated with ammonium hydroxide at about pH-6.9-7. After precipitation, filtration was carried out. The precipitate is medium and heavy rare earth hydroxides and the filtrate was used for precipitation of other rare earths.



Fig. 4 HNO₃ Digestion of Rare Earth Hydroxide

Removal of Neodymium and Praseodymium

The pH of neodymium is 7.31 and pH of praseodymium is 7.35. So, the filtrate after removal of medium and heavy rare earths was precipitated at about from pH-7.3 to 7.4. Then filtration was made. The filtrate includes lanthanum and the precipitate is neodymium and praseodymium hydroxide.

Precipitation of Lanthanum

After removal of other rare earths, the solution was precipitated with ammonium hydroxide at pH-7.9, lanthanum hydroxide was obtained. Then filtration was carried out. The filtrate was then precipitated again at pH-9.6 to get more purify lanthanum oxide. After adding these two precipitates at pH 7.9 and 9.6, this precipitate was digested again with nitric acid. The precipitation of lanthanum hydroxide, stage seven of the flow diagram, is shown in Fig. 5. Then selective precipitation was made according to the above procedure in order to obtain high purity of lanthanum oxide and the precipitation was carried out about three times.



Fig. 5 Precipitation of Lanthanum

After three times precipitation, lanthanum hydroxide was digested with nitric acid and precipitated with oxalic acid. Precipitation of the solution with oxalic acid is shown in Fig.

6. Lanthanum oxalate was obtained and calcined at 1000°C. Then 96% of lanthanum oxide was obtained. It has white color.



Fig. 6 Lanthanum Oxalate after Three Times Precipitation

III. RESULTS AND DISCUSSION

All of the following results are analysed by X-Ray Fluorescence Spectrometer (XRF).

Composition of Monazite concentrate from Moemeik Myitsone Area is shown in Table II.

TABLE II
COMPOSITION OF MONAZITE CONCENTRATE FROM MOEMEIK MYITSONE AREA

No	Element	XRF analysis (%)
1	La ₂ O ₃	13.44
2	P ₂ O ₅	26.73
3	SiO ₂	4.3
4	ZrO ₂	1.36
5	TiO ₂	2.75
6	Fe ₂ O ₃	1.15
7	CeO ₂	27.35
8	ThO ₂	8.14
9	Y ₂ O ₃	1.71
10	Nd ₂ O ₃	3.34
11	Pr ₆ O ₁₁	1.65
12	Other Rare Earths and Associated Minerals	16.22

Composition of Rare Earth Oxides before Cerium Removal
Composition of Rare Earths Oxides before Cerium Removal is shown in Table III.

TABLE III
COMPOSITION OF RARE EARTH OXIDES BEFORE CERIUM REMOVAL

No	Element	XRF analysis (%)
1	La ₂ O ₃	23.05
2	CeO ₂	31.74
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

Composition of Rare Earth Oxides after Cerium Removal
Composition of rare earth oxides after cerium removal is shown in Table IV.

TABLE IV
COMPOSITION OF RARE EARTH OXIDES AFTER CERIUM REMOVAL

No	Element	XRF analysis (%)
1	La ₂ O ₃	41.51
2	CeO ₂	0.23
3	Y ₂ O ₃	4.52
4	Nd ₂ O ₃	40.71
5	Pr ₆ O ₁₁	5.66
6	Sm ₂ O ₃	3.7
7	Gd ₂ O ₃	2.87

Composition of Rare Earth Oxides after Three Times Precipitation

The composition of the rare earth oxides after first precipitation, second precipitation and third precipitation method by X-Ray Fluorescence Spectrometer (XRF) analysis is shown in Table V, VI, and VII.

TABLE V
COMPOSITION OF RARE EARTHS AFTER FIRST PRECIPITATION

No	Element	XRF analysis (%)
1	La ₂ O ₃	65.1
2	Y ₂ O ₃	1.19
3	Nd ₂ O ₃	20.9
4	Pr ₆ O ₁₁	3.37
5	Sm ₂ O ₃	2.29
6	Other Rare earths and Associated Minerals	8.05

TABLE VI
COMPOSITION OF RARE EARTHS AFTER SECOND PRECIPITATION

No	Element	XRF analysis (%)
1	La ₂ O ₃	77.95
2	CeO ₂	0.27
3	Y ₂ O ₃	0.18
4	Nd ₂ O ₃	19.17
5	Pr ₆ O ₁₁	1.65
6	Sm ₂ O ₃	0.05
7	Other Rare earths and Associated Minerals	0.23

TABLE VII
COMPOSITION OF RARE EARTHS AFTER THIRD PRECIPITATION

No	Element	XRF analysis (%)
1	La ₂ O ₃	96.0
2	CeO ₂	0.44
3	Nd ₂ O ₃	1.48
4	Pr ₆ O ₁₁	0.34
5	Other Rare earths and Associated Minerals	2.74

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.

Precipitation Process

There are two process to get lanthanum oxide, solvent extraction process and precipitation process. In the precipitation process, only nitric acid, ammonium hydroxide and oxalic acid were used. In the solvent extraction process, besides nitric acid, oxalic, tributylphosphate (TBP) or PC88A were also needed. Since, the precipitation process has the advantage of time saving and low cost over the solvent extraction process, the precipitation process was used in this study although it gives lower recovery than solvent extraction process.

IV. CONCLUSION

Lanthanum is extracted from Moemeik Myitsone Monazite which contains about 13.44% La₂O₃. 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 precipitation process, ammonium hydroxide was used for precipitation. Precipitation was made for three times. After third precipitation process, 96.0% lanthanum oxide was obtained. So the selective precipitation process gives high purity within shorter time and with lower cost although the solvent extraction process gives higher recovery.

REFERENCES

- [1] N.E.TOPP., 1965. The Chemistry of the Rare-Earth Elements. Amsterdam/London/New York. Elsevier Publishing Company.
- [2] Eugene V. Kleber and Bernard Love., 1963. The Technology of Scandium, Yttrium and the Rare Earth Metals.
- [3] Cuthbert F.L., 1958. Thorium Production Technology
- [4] Gupta C.K. and N. Krishnamurthy.2004. Extractive Metallurgy of Rare Earths, Taylor and Francis, CRC Press Ltd.
- [5] Molycorp, Inc. Cerium, A Guide to its Role in Chemical Technology, Mountain Pass, CA U.S.A.
- [6] Bailar J.C, Urbana J.R , Comprehensive Inorganic Chemistry.
- [7] Hamble, A.Clifford. 1967. Rare Metals Hand Book. 2nd ed. New York, U.S: Robert E.Krieger Publishing Corporation.