

Feasibility of Extraction of Cerium dioxide (CeO₂) from Monazite at Pulmoddai

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Abstract

Monazite concentration in Pulmoddai mineral sand deposit in Sri Lanka is 1.38%. Its Rare Earth Elements (REE) composition is about 61%. Currently, only heavy minerals are separated and cerium rich monazite is discarded. Therefore, the study is focused on finding feasibility of extraction of CeO₂ from Pulmoddai monazite. The research was conducted under four stages, removal of phosphate ions, removal of radioactive elements, purified Rare Earth oxide (REO) preparation and selective separation of CeO₂. The optimum concentration of NaOH solution is found as 80% (w/v)/ 20M. Alkaline digestion was done for 4hrs at 150°C by adding 25 ml of NaOH to 25 g of monazite, followed by acid leaching with 50 ml of 60%(w/v) HCl at 90°C for 1hr. Concentration of 20 g/L (0.22M) oxalic acid should be added to the RE chloride mixture until the complete precipitation of RE oxalates. Purified REO was obtained by calcination at 900°C for 2hrs using RE oxalate precipitated. Purified REO was used to recover CeO₂ by subjecting to selective precipitation. Selective precipitation of CeO₂ was carried out using solid form of KMnO₄ and (15wt%) Na₂CO₃ solution with maintaining average pH value 4 by manual addition of Na₂CO₃ solution ([15 g /100 L]/0.001M).

Keywords: Acid leaching, Alkali leaching, Calcination, Rare Earth Element, Selective precipitation.

1. Introduction

Rare earth elements (REEs) are a group of seventeen metallic elements with chemical similarities, consisting fifteen lanthanides with scandium and yttrium [1]. Despite the term "rare", these elements are comparatively abundant in the earth's crust than most common elements, such as Cu, Pb, Co, and Sn. However, REEs rarely occur in economical concentrations in the

earth's crust making the extraction process complex and expensive [2, 3]. REEs are mainly categorized as light rare earth elements (LREEs) and heavy rare earth elements (HREEs). LREEs are more abundant than HREEs [4].

Over the past few decades (1985-2020), REEs have become vital in the modern-day (2020) life and it is hard to find any modern technology appliance without containing REEs [5]. Unique properties of REEs, such

as magnetic susceptibility, electrical conductivity, solubility, thermal expansion and phosphorescence have resulted in a technological revolution in the past decades (since 1960) [6]. Due to the advancement of modern high technological applications, demand for rare earths (RE) is subjected to a rapid increment, which may cause a surplus RE demand in world market [7].

1.1 REE Potential of Sri Lanka

In Sri Lanka, different geological formations and mineral resources in the Precambrian lithology and soil cover contain significant concentrations extractable REEs, (e.g. mineral sand, clay, carbonates, and gem-bearing sediments) [10]. In 2020, none of above mentioned resources currently being mined to produce REEs. Most resources could be utilized for REE production as a by-product. In this context, the Pulmoddai mineral sand deposit is an important source of REE. Lanka Mineral sand limited (LMSL) producing monazite as a by-product from the deposit provides a great opportunity to extract REEs. Heavy minerals, such as ilmenite, rutile, and zircon are mainly separated and monazite is produced as a by-product.

2. Methodology

2.1 Study area

Pulmoddai mineral sand deposit is nearly four miles in length, approximately 60.96 m wide and estimated to contain approximately 4 million tons of raw sand [11]. The deposit spreads along a beach stretching from Nilaveli 72.42 km, to Mulativu.

Beach mineral sand in Pulmoddai is processed by LMSL for separation of heavy minerals. Thus, nearly 100 tons of monazite is annually produced as a by-product of the process and removed as waste product. It shows that nearly 60 tons of REE can be extracted annually if a proper production process is implemented.

2.2 Sample storage and preparation

Following methods are adopted to store the collected samples as it contains radioactive elements. A desolate place has been selected as sample storage location to avoid exposure to radiation. Samples were stored in concrete blocks and closed with a concrete lid. The particular area was demarcated as a radioactive zone.

Random sampling was utilized in this research. Therefore, the samples for testing was selected randomly from the stored bulk sample.

The radioactivity level of the sample was measured using a Geiger counter by maintaining a distance of 1 m vertically above the sample face using appropriate safety gear.

- Stage1: Removal of Phosphate ions

Particle size 10-400 μm with radioactivity level of 500-900 cpm, crude monazite sand was used as input material in the below mentioned process (Figure 1.) It was subjected to alkaline digestion with 80% (w/v)/20M NaOH for 4hrs at 150°C in an oven by adding 25 ml of NaOH to 25 g of monazite. The sample was subjected to 5 rps (300rpm) magnetic stirring after 2hrs of digestion. The process was repeated five times for different NaOH concentrations (12.5M, 15M, 17.5M, 20M) and the optimum value was found to be 80% (w/v)/20M.

The formed cake was crushed using a glass rod and subjected to 5rps magnetic stirring followed by three times washing with hot water. This washing process is to remove the excess NaOH. Filtration was followed by using Whatman grade 5 filter paper. Filtrate was Na_3PO_4 (aq) and excess NaOH (aq). Filtrate was heated at 140°C for 2 hours until crystallized Na_3PO_4 was generated. Residue was taken as the input material of stage 2.

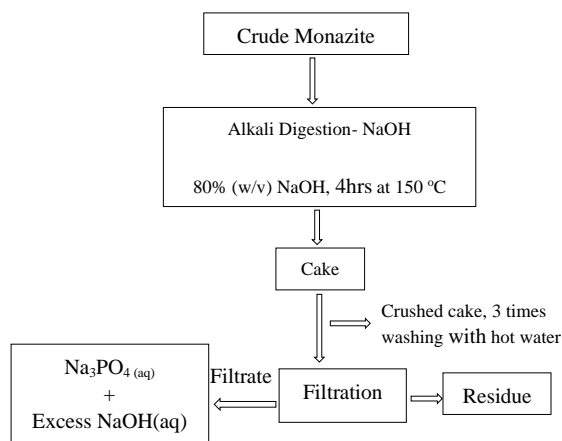


Figure 1: Removal of Phosphate ions

- Stage2: Removal of Radioactive Elements

As shows in the figure 2, the residue was subjected to HCl leaching. 60% (w/v)/16.5M, 25 ml HCl was added to the residue obtained from 25 g of monazite and dried at 90°C in a closed container for 1hr duration followed by filtration of the leached sample.

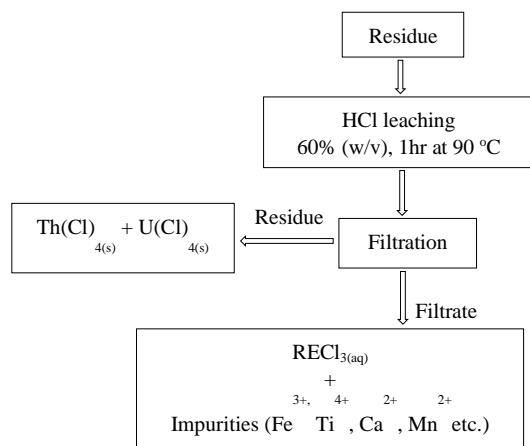


Figure 2: Removal of Radioactive Elements

- Stage3: Purification and Rare Earth Oxides Preparation

As shown in figure 3, 20 g/L (0.22M) of oxalic acid was added to the rare earth chloride with impurities mixture obtained from the process of 25 g of monazite until the completion of precipitation of rare earth oxalates, allowing a 4hr period to accomplish precipitation. Precipitate was subjected to three time washing with diluted oxalic acid. Finally the purified rare

earth oxalates were subjected to calcination process at 900°C for 2hrs under 1atm pressure using a platinum (Pt) crucible in a muffle furnace.

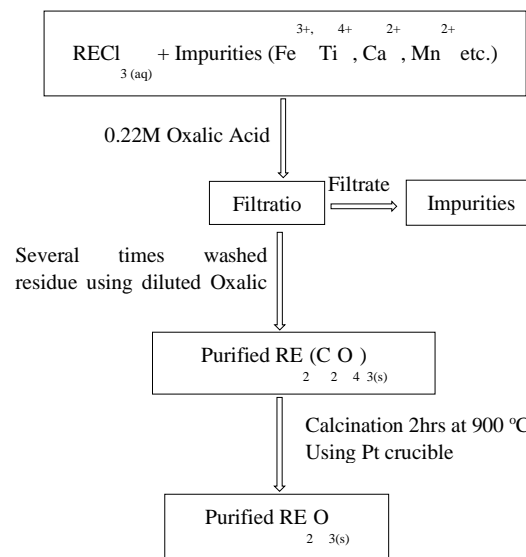
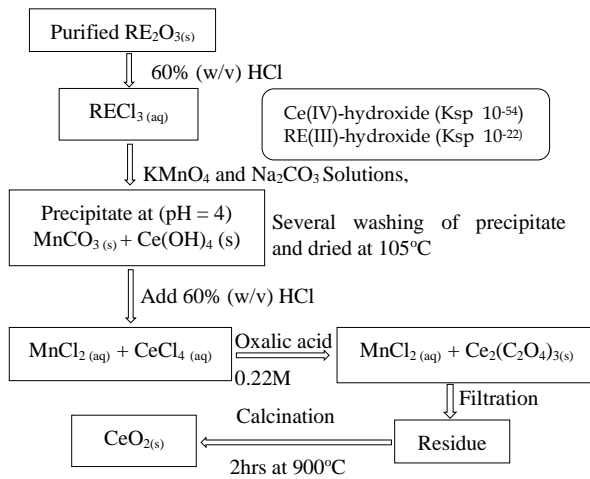


Figure 3: Purification and Rare Earth Oxides Preparation

- Stage4: Selective Separation of CeO₂

The process shown in figure 4 was carried out under 8rps (480rpm) magnetic agitation, at room temperature (25±1°C) under 1 atm pressure using 100 ml of rare earth chloride solution. The oxidation of Ce³⁺ to Ce⁴⁺ was accomplished through the addition of KMnO₄ (0.25 - 1.25 g) to 100 ml of rare earth chloride solution.

The average reaction time was approximately, 60±5 minutes and temperature set to 105±1°C. Precipitation of Ce⁴⁺ was accomplished with the addition of Na₂CO₃ solution (15wt %) in a beaker. The average pH value was controlled at 4 throughout the process by manual addition of a Na₂CO₃ solution ([15 grams /100 L]/0.001M M), dried at 105°C in 1 atm pressure [12]. Finally, the product was calcinated in a Pt crucible for 1hr at 900°C under 1atm pressure in a muffle furnace to produce cerium oxide (CeO₂) [13].



Based on (Renata, et al., 2010) and (Purwani, et al., 2019)

Figure 4: Selective Separation of CeO₂

3. Results and Discussion

3.1 Initial sample analysis

To confirm the REE content in the sample, XRF analysis was carried out for the three monazite samples. The results are shown in Table 1.

Table 1: XRF results of initial crude monazite sample

Type	CN*	Percentage
Major oxides	SiO ₂	14.71
	Al ₂ O ₃	0.21
	K ₂ O	0.04
	CaO	0.4
	TiO ₂	1.5
	MnO	0.03
	Fe ₂ O ₃	12.36
REE	Ce	5.14
	La	2.71
	Y	0.67
	Other elements	
Zr	15.3	
Th	4.58	
U	0.15	
Other		1.05

CN* -Chemical Notation

The table shows the average value of the three samples analyzed. It is confirmed that the samples consist of REEs, namely, Ce, La and Y, and Ce having the highest concentration of the REEs. To confirm P and Nd content, three samples was subjected to a Scanning Electron Microscopy (SEM) analysis. Average

results are shown below in table 2 and figure 5.

Table 2: SEM result of initial monazite sample (Average values)

Element	O	Al	Si	Zr	Th	Ti	Fe	P	Nd	Ce	La
Weight %	37.25	0.15	12.5	21.43	0.67	1.09	1.33	6.87	2.96	10.71	5.03

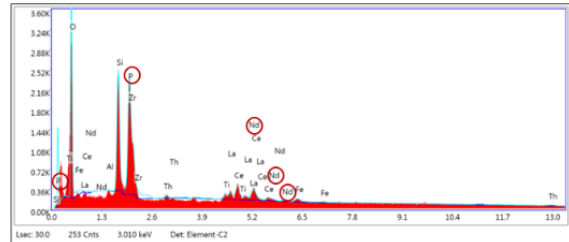


Figure 5: SEM result of initial monazite sample

3.2 Optimum NaOH concentration

NaOH was used for alkaline digestion as it is cheaper than KOH. Therefore, using NaOH would be an economical approach in the industry. The sample consists of REEs and radioactive elements as phosphate compounds. During the digestion these phosphate matrixes are reacted with NaOH [14].

Alkaline digestion process was carried out under five different NaOH concentrations ([50, 60, 70, 80, 90% w/v]/ [12.5, 15, 17.5, 20, 22.5M]) to arrive at the optimum value of concentration of NaOH. NaOH concentration vs. sodium phosphate weight plot is shown in figure 6.

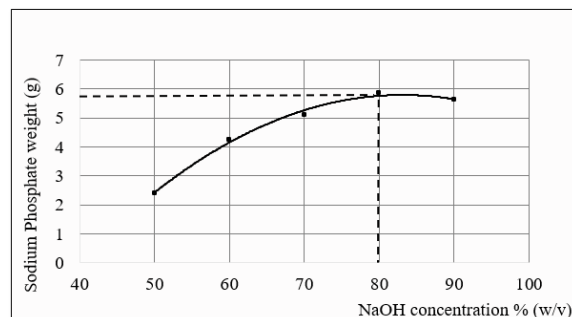


Figure 6: NaOH concentration Vs recovery of Sodium Phosphate Weight

The graphical representation shows that 80% (w/v) NaOH concentration gives the maximum recovery of sodium phosphate.

3.3 Study on the mechanism of washing and crushing

In the process of stage 1, while digesting the sample, it was subjected to 5rps (300rpm) magnetic agitation for 2hrs at 150°C, to facilitate the reaction of most of the phosphate ions (phosphate in the middle of the cake) in the sample. The cake obtained in was crushed using a glass rod and subjected to 5rps (300rpm) magnetic stirring followed by three times washing at 80°-100°C with hot water, without which, the NaOH gradually diffuses into the interior and continues to react with the undissolved REPO₄ in the center by forming RE(OH)_x as in figure 7 [15].

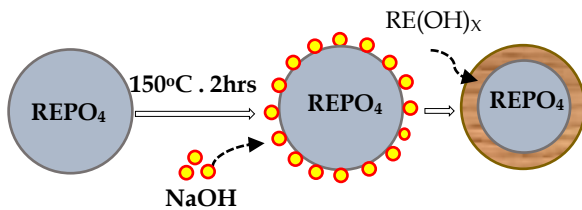


Figure 7: Forming RE(OH)_x

Followed by this, it was subjected to three times washing at 80°-100°C with hot water to remove the unreacted NaOH. Otherwise the unreacted NaOH may produce NaCl in further steps.

After alkaline leaching, the next step was to produce RECl₃. 60% (w/v)/16.5M HCl was added to the residue consisting of RE(OH)₃ and radioactive hydroxides mixture. After acid leaching, the filtrate obtained was Ca²⁺, Mg²⁺, Mn²⁺, Fe³⁺, Al³⁺, and remaining Th⁴⁺, UO₂²⁺, and PO₄³⁻ ions [16]. This solution was crystallized and analysed and result are shown in table 3 and figure 8.

Table 3: SEM result for Composition of Crystallized RECl₃

Element	Na	Cl
Weight %	30.74	36.38

It shows that the solution consists of Na, Cl. At this point it was decided to wash the cake obtained in alkaline digestion process.

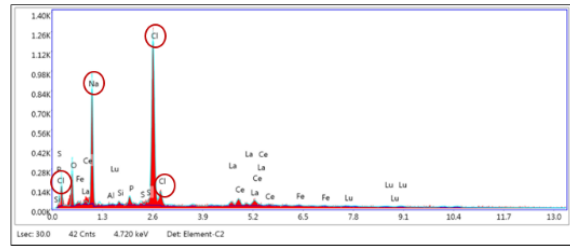


Figure 8: SEM result of Crystallized RECl₃ without washing

Followed by this, analysis of the sample with the washing of the cake was carried out. The SEM result is shown in figure 9.

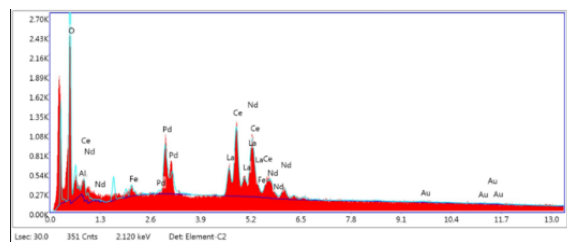


Figure 9: SEM result of Crystallized RECl₃ after washing of crushed cake

3.4 Study on the radiation levels in each step

As the monazite sample consists of radioactive elements (Th and U), their removal in the initial process was essential to minimize the effect of radioactivity in the following steps. The average radiation levels are shown in table 4.

Table 4: Radioactive level in bulk and sample

Step	Radiation level (Average Values)
Bulk	500-900 cpm
Sample of 25g	80-150 cpm

To assess the degree of elimination of radioactivity the initial sample was analyzed as mentioned above, with the final radioactive residue using the Geiger counter and XRF analysis. The average values are shown in table 5.

The "Th" content in the cake has been enriched compared with the initial sample, but not in the HCl leached residue compared with the cake. The "U" content in the cake has not been enriched

compared with the initial sample, but, enriched in HCl leached residue compared with the cake. According to the results obtained, it shows that all radioactivity has not been removed after the HCl leaching. Th and U content were analyzed at 45,591ppm 1,594ppm respectively. The remaining radioactivity elements in the rare earth chloride solution have been removed after the addition of oxalic acid to the solution.

Table 5: Dilution of the radioactive elements through the process

3.5 Analysis of the final product

	Radioactive Concentration (ppm)		
	Initial Sample	Cake (RE(OH) ₃ + Th(OH) ₄ + U(OH) ₄)	HCl Leached Residue
Th	41,991	49,637	45,591
	↩ Enriched ↪		↩ Not Enriched ↪
U	1,409	1,212	1,594
	↩ Not Enriched ↪		↩ Enriched ↪

After the purification process with oxalic acid, rare earth oxide sample was subjected to SEM analysis. The result is as shown in table 6 and figure 10.

Table 6: SEM Analysis of Purified RE₂O₃

Element	Ce	La	Nd
Weight %	40.06	14.78	19.08

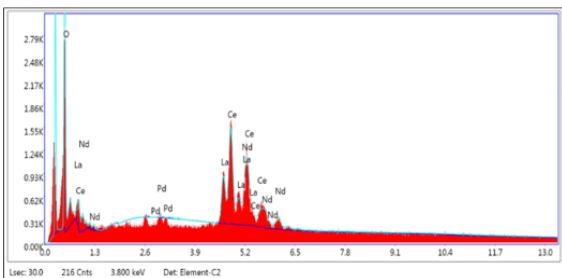


Figure 10: SEM Analysis of Purified RE₂O₃

Results shown in figure 10 shows the RE oxide sample does not contain impurities. The process is of significance as the product does not contain impurities and

therefore, will create a demand fetching a good market price.

In the selective precipitation step, KMnO₄ and Na₂CO₃ were used. The solid form of KMnO₄ was used as an oxidizing agent. To enable selective precipitation, Ce³⁺ should oxidize to Ce⁴⁺. [15 grams/100L]/0.001M Na₂CO₃ was used as a precipitating agent after oxidation.

SEM analysis was carried on the final product of selective separation. Results in table 7 and figure 11 show the sample does not consist only of Ce, but Nd and La. It shows that chemical selective precipitation is not accurate and effective. It is due to this fact, that solvent extraction is adopted to do selective precipitation of REEs.

Table 7: SEM Result for Final CeO₂ Product

Element	La	Ce	Nd
Weight %	21.50	44.82	14.32

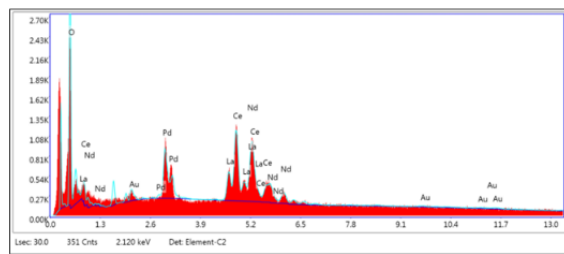


Figure 11: SEM Result for Final CeO₂ Product

3.6 Effect of particle size on RE₂O₃ recovery

Laser particle size analysis was conducted on three samples. Figure 12 shows average particle size range is from (10 to 400) μm.

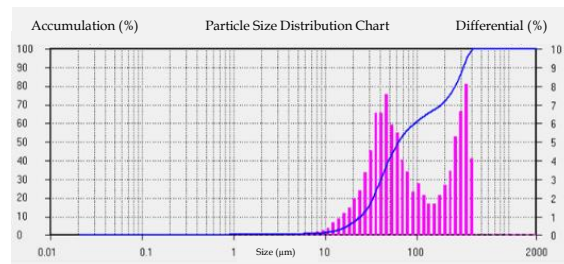


Figure 12: Laser particle size analysis of sample 1

How the particle size affected the recovery of purified rare earth oxides was tested. Table 8 shows that maximum recovery can

be obtained using a particle size under 63 μm .

Table 8: Effect of Particle Size on Rare Earth Oxide Recovery

Particle Size	Recovered RE_2O_3 weight (g) from 25g of initial Sample
Original sample (10 - 400) μm	1.742
Sieved from 63 μm	3.125

4. Conclusions

The first conclusion drawn from experimental results is that 80% (w/v)/20M NaOH is the optimum concentration to digest Pulmoddai crude monazite. The same procedure was followed for 50, 60, 70, 80 and 90% (w/v) concentrations and the value of 80 was obtained as the value that results in the maximum phosphate recovery.

Following alkali digestion, it is required to carry out 5rps (300rpm) magnetic stirring during the process to facilitate the reaction of most of the rare earth phosphates. The sample was digested for 4 hrs at 150°C. Therefore, stirring is needed after 2hrs. The cake obtained after alkali digestion must be subjected to three times washing with 80°-100°C hot water before subjected to acid leaching. It is to enable the removal of unreacted NaOH. Otherwise, it may lead to produce NaCl in the process.

It is concluded that 60% (w/v)/16.5M HCl acid is an effective leaching medium when removing the radioactive elements in the initial sample. Most of the Th and U has been removed as shown in table 5.

In the process, oxalic acid was used as the purifying agent of rare earth chlorides and the results obtained show that it is a very accurate and effective process. It is concluded that oxalic acid is preferred to produce purified rare earth chlorides. For the selective separation of CeO_2 , chemical separation method was used. Results show that it is feasible to extract CeO_2 with this separation method.

This overall process was followed for the initial sample as well as 63 μm sieved sample. The final weight values of CeO_2 gave average value of 3.125 g for sieved sample. As initial sample gave 1.742 g. So, can conclude the process is optimum when particle size is under 63 μm .

5. Recommendations and Further Studies

With the available facilities, the analysis of the research was limited to XRF and SEM instrumentation. However, it is recommended to use ICP-MS or ICP-OES due to the high level of sensitivity.

For further studies it is suggested to do this process under exact pH level (pH=4) for a better result. Solvent extraction using Tributyl phosphate (TBP) and stripping of oxalic acid concentration, also can be recommended for the selective separation of CeO_2 . By using CeO_2 extracted, using the methodology adopted, Ce metal should be recovered using an appropriate method.

Moreover, the removal process of radioactive concentrates should be optimized to produce the Th and U as mass scale by-products by treating Th and U phosphates. Further, it is recommended that the process should be developed to obtain phosphate as a mass scale by-product by treating sodium phosphate.

As monazite is discarded by LMSL as tailings, it is recommended to subject this waste monazite to value addition. This can be carried out at Pulmoddai processing plant by upgrading it to process monazite for REEs as well as for radioactive (Th,U) products and phosphate fertilizers. With the upgrading of available infrastructure, LMSL is in a position to involve itself fully play a major role, in the Sri Lankan mineral exporting industry earning significant amount of foreign exchange by exporting purified REO alone. It is noted that purified REO has very high in the international market.

It is recommended to initiate action to convert the monazite bearing tailings currently stored in the Pulmoddai plant premises into a profitable product. To that

conducting an economic feasibility study is a must.

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