Extraction of Rare Earths from Monazite in Pulmoddai Deposit

Witharana WPWS, Prabath DHL, Madushanka RS and *Rohitha LPS and Dissanayake DMDOK

Department of Earth Resources Engineering, University of Moratuwa, Sri Lanka

*Corresponding author – rohitha@uom.lk

Abstract

Rear earth elements (REEs) have considerable demand in the world and higher market value due to various applications, emerging economies, and continuous depletion of rare earth (RE) metals. Monazite is a perfect source for REEs (61%) and consists of RE and Thorium Phosphate. The Phosphate component was removed by alkaline leaching using NaOH (80 W/V%) at 1800° C for 4 hours at 500 rpm. Thorium was removed by acid leaching using (60 W/V%) HCl at 90° C for 1hour at 500 rpm and 15% pulp density. The solvent extraction method was carried out to separate and purify RE-Oxides from other impurities. 50% Tributyl phosphate (TBP) in kerosene was used as an organic phase with available facilities, and an experiment was done for phase ratio 1 and phase ratio 2, for 3, 6, and 12 minutes of contact time. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was done for elemental analysis. Most abundant REEs in Monazite were Cerium (39%), Lanthanum (20%), Neodymium (12%) and Praseodymium (4%). The main objective of this research was to identify an industrial-level efficient method for separating and purifying RE from Monazite. Economically viable industrial level extraction of REEs was obtained when the phase ratio equals one and 3 minutes contact time.

Keywords: Acid leaching, Alkaline leaching, Dephosphorization, Solvent extraction, Rear earth

1. Introduction

REEs are a group of 17 elements which are 15 Lanthanides series (Atomic number = 57 to 71), Scandium (Atomic number = 23), and Yttrium (Atomic number = 39) in the periodic table. Based on their ionic radius, REEs are mainly classified into two groups as Light REEs (LREEs) and Heavy REEs (HREEs). LREEs have consisted of La to Sm (La, Pr, Nd, Sm), and HREEs have consisted of Eu to Lu (Eu, Gd, Tb, Y, Dy, Lu). These elements are referred to as REEs not only because they are moderately abundant in nature but the concentration of that element is very low.

In the past, REEs were not in high demand due to extraction difficulties. With time, various methods were experimented and utilized to extract REEs efficiently and effectively. The world's energy requirement is steadily rising over time. Thus the requirement of energy is fulfilled by oil, coal, fossil fuels, and natural gas.

Therefore, the amount of CO_2 emitted to the atmosphere increases, and it has various adverse effects. Thus the requirement for a green energy system is increased. Furthermore, economic risk, oil price volatility, and the energy crisis have already created the requirement for a green energy system. Further, demand for REEs is increased due to their applications in many fields such as electronic, medical, military, energy, and manufacturing. Thus, the demand for the REEs market is significantly increased and created a higher request for the global production of REEs.

REEs are found in six ores such as Bastnasite, Monazite, Xenotime, Loparite, Apatite, and ion adsorption clay. Monazite is a perfect source for REEs, specially Cerium (20–30% Ce_2O_3), Lanthanum (10–40% La_2O_3), and Neodymium [1]. Monazite shows radioactive properties due to the presence of Thorium and uranium. In 2020, the amount of global production of REO was 240,500 metric tons. China is the world-leading REEs producer. They produce 140,000 metric tons of Rare Earth Oxides (REO) and have increased their production to 90% of world production. In 2020, Main REEs deposits are located in various countries in the world such as China, Russia, Australia, the USA, Canada, Brazil, Green island, South Africa, India, etc. [1].

Although not very large, Sri Lanka also has some potential to have REEs due to the presence of several RE-sources such as Monazite, Apatite, and gem bearing ores. Although it has some potential to occur Bastaesite and Xenotime deposits with Sri Lankan geology, still those deposits were not found. Thus, it is needed to carry out a proper exploration process to identify and profitably extract these elements.

Pulmoddai beach sand deposit is the major Monazite deposit in Sri Lanka. Although many researchers have developed several methodologies to extract REEs, Sri Lanka has not been able to develop a successful industrial-level methodology to extract REEs yet. Pulmuddai mineral sand contains Ilmenite, Garnet, Rutile, Zircon, Spinal, Sillimanite and Monazite. Ilmenite and Rutile are separated as the main mineral, and Monazite is a by-product. Monazite is consisted of Thorium and REEs (Cerium (28%), Lanthanum (15%), Neodymium (10%), Promethium (3%), Samarium (2%), Gadolinium (2%) and Yttrium (1%)) Phosphates. Monazite concentration in Pulmuddai beach sand is 1.38%, and Monazite has about 61% of REEs [7]. Therefore, these monazites can be utilized effectively by extracting REE.

Several physical separation methods are used to concentrate REEs bearing minerals, such as gravity separation, electrostatic separation, or magnetic separation. Concentrated REEs bearing minerals should be subjected to chemical or physicochemical methods to extract REEs with considerable purity. Main conventional REEs extraction technologies are fractional step method, fractional extraction, ion exchange, etc. With the development of technology, bio-hydrometallurgical method, solvent extraction method, a hydrometallurgical method has a tendency to use to extract REEs. Due to the high chemical and physical stability, the economical extraction and processing of REEs are difficult and costly.

1.1 Physical separation of Monazite

The suitable physical separation method depends on their mineralogical and chemical composition from location to location. Gravitational separation and wet high-intensity magnetic separation (WHIMS) methods are the most commonly used methods for concentrating Monazite. Minerals that have low specific gravity can move easily long distances forward. Minerals that have high specific gravity remain moving a short distance. By applying different intensity magnetic fields, minerals are separated as ferromagnetic, diamagnetic and paramagnetic from each other. The recovery percentage varies with the granule size, the feed rate, the electrode configuration, the high-voltage level and the speed of the roller. All those factors should be optimized to get maximum recovery. For high-grade Monazite mixtures (≥33.3 wt.%), the field intensity investigated were not enough to completely recover. For low grade (Monazite) mixture (≤10 wt.%) WHIMS method is most suitable with higher magnetic field intensity (high-voltage level– 25 kV, roll speed - 60 r/min, feed rate– 1.5 kg/h intensity≥1.08 T).

1.2 Treating with Hydrogen Peroxide

The Monazite can consist of organic matters, and Monazite is treated with Hydrogen Peroxide ($H_2O_{2\ (aq)}$) for several hours to remove organic matters.

1.3 Dephosphorization

RE-Phosphate is a crystalline Phosphate mineral. Due to the high lattice energy of the P-O bond and RE-O bond, $RE(PO_4)_3$ has high thermal and chemical stability. Thus it is unable to decompose even at high temperatures. Thus hydrometallurgical methods or pyrometallurgical methods are used to recover REEs from Monazite. In various researches were done direct leaching of Monazite by using acidic leaching and alkali leaching methods. Sulfuric, Hydrochloric and Nitric acids etc., are used as acid solutions, while Sodium hydroxide, Potassium hydroxide, Sodium peroxide, Potassium chloride, Sodium carbonate, Calcium hydroxide, etc. are used as alkali solutions. Optimum conditions should be used for effective dephosphorization.

Acidic digestion process

$2REPO_{4(s)} + 6H^+ \longrightarrow 2RE^{3+}{}_{(s)} + 2H_3PO_4$

Alkaline digestion process

$REPO_{4(s)} + 3\ OH^- \longrightarrow RE(OH)_{3(s)} + PO_4{}^{3-}$

Experiments were done using different parameters for direct leaching processes of Monazite concentrate by acid or alkali leaching to recover REEs. Table 1 shows the summary of direct leaching processes of Monazite concentrate using acid or alkali to recover REEs.

Table 1: Direct leaching processes of Monazite concentrate using acid or alkali to recover REEs.

Medium	Temperature (^0C)	Time (h)	Reference
(93–96% H_2SO_4)	200–220	3	[2]
50% NaOH (w/v)	170	4	[3]
Na_2CO_3 1:1 (w/w)	900	2	[4]
NaOH 1:1w/w	400	2	[4]
50% NaOH (w/v)	170	4	[5]
80% (w/v) NaOH	150	4	[6]
80% (w/v) NaOH	150	4	[7]

Here are some advantages of using the NaOH digestion process;

- Can recover Tri-Sodium Phosphate as a by-product which is used as fertilizer [4].
- Monazite is transformed into the RE-Hydroxide. Thus RE- Hydroxide will easily dissolve in acid after removal from the supernatant solution of alkaline Phosphates.
- Chemical reactions do not produce any liquid wastes [8].
- No chance to emit acidic gasses to the environment and low maintenance cost [4].
- In the acidic leaching method, separation of Th and RE's is poor, and maintenance cost is high [4].

The disadvantage of the alkaline digestion method is the requirement of a huge amount of NaOH and badly affect the filtration process due to excess NaOH from crystalline and blocking the filtration paths.

1.4 Acid Leaching

Various acids are used for leaching and removing radioactive components such as HNO_3, HCl, H_2SO_4 etc. HCl is the best leachate because it removes the radioactivity component at the beginning and makes it a safer manner to continue the entire process. There are several concentrations, temperature, and time was used in experiments. All the REEs and associated minerals are dissolved in an acidic solution, and Thorium and Uranium remain as residue. The residue is contained by Chlorides form of Thorium and Uranium.

$$RE(OH)_{3(s)}+3HCl_{(aq)} \rightarrow RE(Cl)_{3(aq)}+3H_2O_{(aq)}$$

$$Th(OH)_{4(s)}+4HCl_{(aq)} \rightarrow Th(Cl)_{4(s)}+4H_2O_{(aq)}$$

$$U(OH)_{4(s)}+4HCl_{(aq)} \rightarrow U(Cl)_{4(s)}+4H_2O_{(aq)}$$

1.5 Solvent Extraction

Purity and quality are mainly considering factors for the economic value of the individual REEs. There are some impurities in acid/alkaline solution such as Ca^{2+}, Pb^{2+}, Fe^{3+} and $A1^{3+}$, which decrease the quality and economic value for REEs. Solvent extraction is the best method for removing those impurities and obtaining REEs with considerable purity. Similar chemical and physical properties make it difficult to separate individual REEs. But solvent extraction method is reported as the best method for selectively extracting individual REEs.

Distribution ratio (D) and separation factor (SF) are used to determine the extraction possibilities and extraction behaviour. These are defined by equations 1 and 2 when C_0 is the initial concentration and C is the final concentration. The distribution ratios of metal ion 1 and metal ion 2 are defined as D1 and D2 [10].

$$D = \frac{(C0 - C)}{C} \qquad (1)$$

$$SF = \frac{D1}{D2} \qquad (2)$$

Although industrial-level solvent extraction was begun around 1960, it was difficult to isolate a single REEs due to similar physical and chemical properties of individual REEs. The ion exchange method was the only practical method that could extract REEs at the industrial level before 1960.

At present, the solvent extraction method is widely used because it has preferably commercial technology, simple, high capacity, low operating cost, fast kinetics, and high selectivity. The ion exchange method is used only to obtain a small amount of high purity REEs, and it can use for laboratory-scale extractions. Several amines are reported to extract REEs in literature such as TBP, TBA, DOA, D2EHPA, phosphinic acid (Cyanex 272) etc. [11]. When atomic number increase, the most frequently used extractant which used to separate REEs is TBP because extractants are in operation, safety and economically viable. Kerosene is used as an organic diluent. TBP is dissolved in kerosene to prepare an organic phase solution. Two phases of organic and aqueous mixed in a breaker with mechanical stirring. After complete mixing, two phases are separated using a conical separating funnel.

2. Methodology

Monazite sample was directly taken from the Lanka Mineral Sands Limited, which was separated in their processing stage. The initial radioactivity of the sample was measured by the RADALERT100X Giger counter.

2.1 Abundance of REEs in Monazite.

0.5 g of Monazite sample was digested with H_2O_2 (1 ml), HNO_3 (3 ml) and HCl (1 ml) and heated at 200° C for 15 minutes at 1 atm to obtain an abundance of REEs in Monazite.

2.2 Organic matters percentage

14 g of Monazite sample was weighted and proceeded using Hydrogen peroxide ($H_2O_{2\,(aq)}$) to determine organic matter percentage. Hydrogen peroxide was added

to the sample and kept in the fume hood for three hours at 30° C (room temperature) 1 atm (atmospheric pressure) to remove organic matter. The amount of organic matter was obtained by weight difference of the initial weight of the sample and weight of the sample after process with Hydrogen peroxide.

2.3 Monazite Dephosphorization

Three Monazite samples, 30 g for each, were weighted and treated with NaOH (80% W/V) at 180° C for 4 hours. A magnetic stirrer was used at 500 rpm to mix the sample well. After 4 hours sample was washed with hot distilled water several times and filtered using filter paper.

2.4 HCl leaching

Precipitation was leached with HCl (60% w/v) at 90° C for one hour at 500 rpm at 15% pulp density, and samples were filtered using filter paper.

2.5 Solvent extraction

Filtrate solution was put into two beakers of equal volumes. One sample was tested for phase ratio 1, and the other sample was tested for phase ratio 2 to determine the optimum phase ratio. The organic solution was prepared as 50% TBP in kerosene. $RECl_3$ solution was striped with 1M H_2SO_4, and the striped aqueous phase was mixed with organic phase (50% TBP in kerosene) for both phase ratios 1 and 2 in the separatory funnel at 30° C (room temperature) at 1 atm (atmospheric pressure). The stopwatch was started as soon as stopping mixing, and samples were taken from the aqueous phase after 3, 6 and 12 minutes.

3. Result

3.1 Abundance of REEs in Monazite

Initial radioactivity was measured as 40 – 140 CPM, and particles were laid in between 10 – 400 µm. ICP-MS analysis was carried out to determine the ppm level of REEs for the initial Monazite samples. The average ppm level of REEs in Monazite is reported in Table 2.

Table 2: Average ppm level of REEs in Monazite.

REE	Percentage from Total REE (%)	Level (ppm)
La	19.7	4790.0
Ce	38.7	9377.3
Pr	4.0	981.5
Nd	12.4	3002.2
Sm	2.0	492.8
Eu	0.2	56.1
Gd	5.4	1318.8
Tb	0.4	95.4
Dy	1.1	276.3
Ho	0.2	49.6
Er	0.7	167.9
Tm	0.0	10.6
Yb	0.4	86.9
Lu	0.1	13.1
Th	14.2	3453.1
U	0.4	89.1

3.2 Organic matters percentage

Percentage of the organic matters in the sample = 0.86 %.

3.3 Monazite Dephosphorization

ICP-MS analysis was carried out for three samples from $Na_3PO_{4(aq)}$ solution, and Table 3 shows the average ppm level of REEs in the $Na_3PO_{4(aq)}$ solution.

Table 3: Level(ppm) of REEs in $Na_3PO_{4(aq)}$ solution.

REE	Level (ppm)	REE	Level (ppm)
La	0.2678	Dy	0.038
Ce	0.708	Ho	0.004
Pr	0.231	Er	0.032
Nd	0.711	Tm	0.001
Sm	0.038	Yb	0.005
Eu	0.003	Lu	0.012
Gd	0.238	Th	0.134
Tb	0.018	U	0.957

3.4 HCl leaching

ICP-MS analysis was carried out for three samples from $RE(Cl)_3$ solution, and Table 4 shows the average ppm level of Thorium before and after HCL leaching.

Table 4: Level (ppm) of Thorium before and after HCl leaching.

	Before HCl leaching	After HCl leaching
Level(ppm) of Thorium	3,453	54

3.4 Solvent extraction

Figure 1 shows the total REEs extracted from the aqueous phase after solvent extraction in 3, 6 and 12 minutes. Figures 2 and 3 show the ppm level of REEs in the aqueous phase after solvent extraction when the phase ratio is one and two. Figure 4 shows the Individual REEs percentage in the initial and after solvent extraction process when the phase ratio equals one.

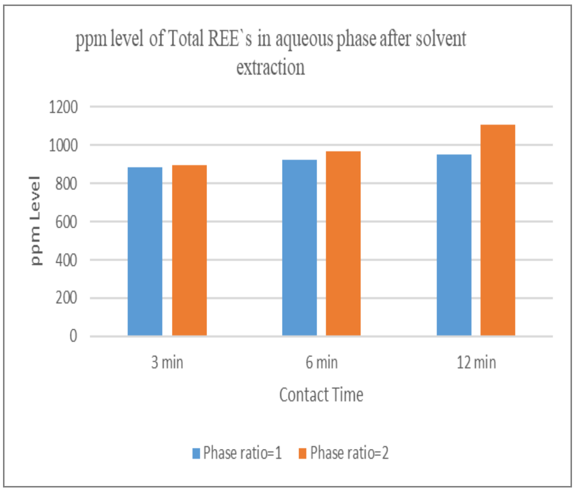

Figure 1: Level (ppm) of Total REEs in the aqueous phase after solvent extraction.

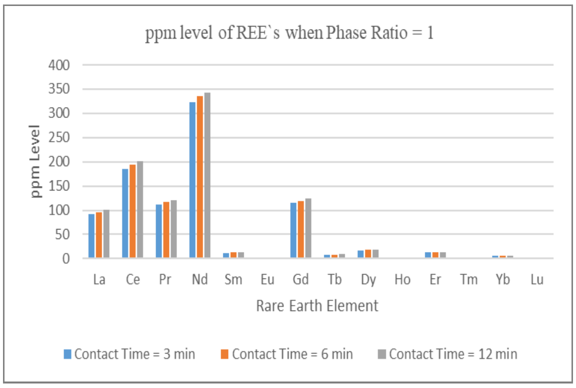

Figure 2: Level (ppm) of REEs in the aqueous phase after solvent extraction when phase ratio is one.

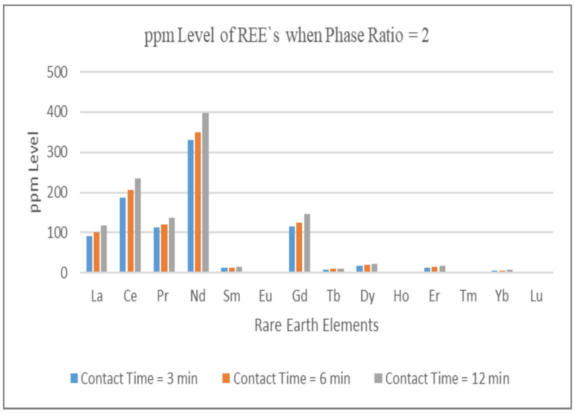

Figure 3: Level(ppm) of REEs in the aqueous phase after solvent extraction when phase ratio is two.

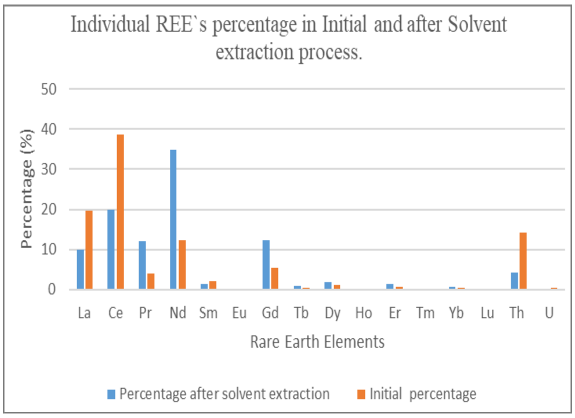

Figure 4: Individual REEs percentage in initial and after the solvent extraction process.

4. Discussion

4.1 Abundance of REEs in Monazite

The most abundant REEs were Cerium (39%), Lanthanum (20%), Neodymium (12%) and Praseodymium (4%). Therefore, Pulmuddai Monazite is a good source for Cerium, lanthanum and Neodymium.

4.2 Determination of organic matters in sample

The presence of organic matter in the Monazite sample was 0.86%. Thus the possibility of having the organic matter in Monazite is negligible.

4.3 Monazite Dephosphorization

Equations Monazite was digested with NaOH and resulted in $RE(OH)_3$, $Th(OH)_3$ precipitation with Na_3PO_4 filtrate and Na_3PO_4 was removed by filtering.

$$REPO_{4(s)} + 3NaOH_{(aq)} \rightarrow RE(OH)_{3(s)} + Na_3PO_{4(aq)}$$

$$Th_3(PO_4)_{4(s)} + 12NaOH_{(aq)} \longrightarrow 3Th(OH)_{4(s)} + Na_3PO4_{(aq)}$$

Extra NaOH and Na_3PO_4 were removed from the sample by washing hot distilled water. $RE(OH)_3$ and $Th(OH)_4$ cake remained on filter paper. According to the ppm level of REEs and Th in the Na_3PO_4 solution (Table 3), The amount of REEs passed through the filter paper to Na_3PO_4 solution was small enough to be ignored. Hence, the Phosphate component was successfully separated from REEs and removed from the Monazite.

4.4 HCl Leaching

$RE(OH)_3$ and $Th(OH)_4$ reacted with HCl and formed $RECl_3$ and $ThCl_4$. $ThCl_4$ was precipitated, and $RECl_3$ remained in the filtrate. So radioactive Th components were successfully separated from REEs.

$$RE(OH)_{3(s)} + 3HCl_{(aq)} \longrightarrow RE(Cl)_{3(aq)} + 3H_2O_{(aq)}$$

$$Th(OH)_{4(s)} + 4HCl_{(aq)} \longrightarrow Th(Cl)_{4(s)} + 4H_2O_{(aq)}$$

According to Table 4, the ppm level of Th after HCl leaching is very low. Thus almost all the Thorium ions were precipitated as $Th(Cl)_4$.

4.5 Solvent extraction

According to Figure 1, the ppm level of the aqueous phase for REEs was not significantly different for phase ratios one and two. But ppm level of REEs in the aqueous phase was much higher when the phase ratio was equal to two rather than one. Thus higher number of REEs were extracted by an organic phase when the phase ratio is equal to one. It was economically viable extracting REEs in phase ratio one due to high expensive process of preparing organic phase. In phase ratio two, waste generation is high, and waste disposal expenses also increase. In our research, we consider about extraction of REEs on an industrial scale. Thus it is better to do solvent extraction in phase ratio one.

In phase ratios, one (Figure 2) and two (Figure 3), the minimum ppm level for Lanthanum, Cerium and Neodymium in the aqueous phase was obtained when contact time equals 3 minutes. Thus most of the Lanthanum, Cerium Neodymium ions are extracted by an organic phase when contact time is 3 minutes.

Individual REEs percentage in initial sample and after Solvent extraction in phase ratio one was shown by Figure 4. The abundance of Neodymium and Gadolinium after solvent extraction is higher than the abundance of Neodymium and Gadolinium in the initial sample. Thus this method is most suitable for Neodymium and Gadolinium due to the well extraction of Neodymium and Gadolinium.

5. Conclusions

Most abundant REEs in Monazite, were Cerium (39%), Lanthanum (20%), Neodymium (12%) and Praseodymium (4%). Monazite does not need to process with Hydrogen Peroxide ($H_2O_{2\ (aq)}$) in REEs productions due to the very low possibility of having organic matters. Several steps were done to extract REEs from Monazite in our research methodology. First, Monazite ore (RE-Phosphate) was digested with NaOH (80 % w/v) at 180° C for 4 hours at 500 rpm when the particle size of Monazite was laid in between 10 - 400 µm. Then, RE-Hydroxide (solid) and Thorium-Hydroxide (solid) was precipitated, and $Na_3PO_{4(aq)}$ was removed by filtering. In the second stage, the precipitated cake was leached with HCl (60% w/v) acid at 90° C for one hour at 500 rpm when the pulp density was maintained as 15%. Then RE-Chloride and Thorium-Chloride(solid) was formed. Undissolved Thorium- Chloride was removed from RE-Chloride$_{(aq)}$ by filtering. In the third stage, REEs were extracted by the solvent extraction method. 50% TBP in kerosene were used as the organic phase at 30° C (room temperature) and 1 atm (atmospheric pressure). Phase ratio one was the best and economically viable for industrial level REEs extraction from Monazite. Most of the Lanthanum, Cerium Neodymium ions were extracted by an organic phase when contact time was 3 minutes. This methodology is mostly suitable for Neodymium and Gadolinium due to the well extraction of Neodymium and Gadolinium.

Acknowledgement

We would like to express our gratitude to Dr. LPS Rohitha, Dr. DMDOK Dissanayake, two senior lecturers in the Department of Earth Resources Engineering for continuous supervision for each step of our research. Our special thanks go to Dr. GVI Samaradivakara, Head of the Department, academic and non-academic staff members of the Department of Earth Resources Engineering, University of Moratuwa, for helping us to succeed in our research.

References

[1] N. Dushyantha et al., 'The story of rare earth elements (REEs): Occurrences, global distribution, genesis, geology, mineralogy and global production', Ore Geol. Rev., vol. 122, no. January, p. 103521, 2020, DOI: 10.1016/j.oregeorev.2020.103521.

[2] S. R. Borrowman and J. B. Rosenbaum, 'Recovery of thorium from a Wyoming ore'. 1961.

[3] R. Panda et al., 'Leaching of rare earth metals (REMs) from Korean monazite concentrate', J. Ind. Eng. Chem., vol. 20, no. 4, pp. 2035–2042, 2014, DOI: 10.1016/j.jiec.2013.09.028.

[4] A. Kumari, R. Panda, M. K. Jha, J. R. Kumar, and J. Y. Lee, 'Process development to recover rare earth metals from monazite mineral: A review', Miner. Eng., vol. 79, pp. 102–115, 2015, DOI: 10.1016/j.mineng.2015.05.003.

[5] Z. Zhang, Q. Jia, and W. Liao, Progress in the Separation Processes for Rare Earth Resources, vol. 48. 2015.

[6] U. Kgi, C. Sadk, L. P. . Rohitha, and D. M. D. O. . Dissanayake, Selective Precipitation of Lanthanum and Neodymium oxides from Pulmoddai Monazite, Sri Lanka. 2021.

[7] U. Rasanjali, D. Shanmugam, N. Dushyantha, N. Batapola, D. M. D. O. . Dissanayake, and L. P. . Rohitha, 'Feasibility of Extraction of Cerium dioxide (CeO_2) from Monazite at Pulmoddai', Jan. 2021.

[8] W. Kim, I. Bae, S. Chae, and H. Shin, 'Mechanochemical decomposition of monazite to assist the extraction of rare earth elements', J. Alloys Compd., vol. 486, no. 1–2, pp. 610–614, 2009, DOI: 10.1016/j.jallcom.2009.07.015.

[9] Z. Zhu, Y. Pranolo, and C. Y. Cheng, 'Separation of uranium and thorium from rare earths for rare earth production - A review', Miner. Eng., vol. 77, pp. 185–196, 2015, DOI: 10.1016/j.mineng.2015.03.012.

[10] F. Xie, T. A. Zhang, D. Dreisinger, and F. Doyle, 'A critical review on solvent extraction of rare earths from aqueous solutions', Miner. Eng., vol. 56, pp. 10–28, 2014, DOI: 10.1016/j.mineng.2013.10.021.

[11] T. Liu and J. Chen, 'Extraction and separation of heavy rare earth elements: A review', Sep. Purif. Technol., p. 119263, 2021, DOI: https://doi.org/10.1016/j.seppur.2021.119263.