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EXPLORING THE POTENTIAL OF RARE EARTH ELEMENT RECOVERY FROM MONAZITE

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Rare earth elements (REEs) are a group of 17 chemically similar elements that are essential for a wide range of modern technologies. One of the main sources of REEs is monazite, which contains cerium, lanthanum, neodymium, and other REEs. The increasing demand for REEs, driven by the growth of technology and renewable energy industries, makes it imperative for the industry to develop new methods for the extraction and separation of these critical elements. The focus of the study is to extract rare earth element (REE) hydroxides from a monazite ore originating from the Jolotca-Ditrău region of Romania.

The process focuses on chemical purification to get REE hydroxides and eliminate uranium and thorium. Chemical purification involves leaching with NaOH, dissolving in HCl, extracting with HDEHP/kerosene, and precipitating REE hydroxides with NH_4OH, resulting in a 203.8 g (46.28 %) of REE hydroxides and ~0,22g Th hydroxide retained in the organic solution.

Keywords: Rare earth elements, monazite, primary resources, NaOH leaching, liquid-liquid extraction, Th and U removal.

1. Introduction

The increasing demand for rare earth elements (REEs) in various high-tech industries has led to a renewed interest in finding primary resources and developing efficient extraction technologies [1, 2].

Due to their unique electronic and magnetic properties, rare earth elements (REEs) have become essential for a wide range of modern technologies, such as smartphones, electric vehicles, wind turbines, and more. They are also used in the production of catalysts, ceramics, glass, and phosphors [2–5]. Currently, China holds one-third of the world's REE reserves and is also the global leader in REE

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exploitation and production. The main global reserves belong to China, Vietnam, Russia, and India, which together account for approximately 130 million tons. REE resources come from four geological environments: carbonatites, alkaline igneous systems, ion-adsorption clay deposits, and monazite-xenotime-bearing placer deposits [3].

The European Union, through the European Raw Materials Alliance, as well as the EURARE and ASTER projects, has shown its interest in critical raw materials, including REE, in order to reduce critical dependencies and secure its supply chains [6].

REEs are often divided into two groups: light REEs (LREEs) including cerium, lanthanum, and neodymium, and heavy REEs (HREEs) which include dysprosium, erbium, and yttrium.

Among these, neodymium and dysprosium are considered the most critical REEs for modern technologies due to their unique properties and wide range of applications [1, 6–8]. Rare earth elements (REEs) are found in various minerals, however, the primary source of REEs is the mineral monazite [(REE)PO_4] [3, 6, 9, 10]. Monazite is a world source of both REEs and thorium (Th) elements, and it can vary in color from yellow to brown or red [11, 12]. These deposits can be found in beach sands, as well as in certain types of igneous rocks, such as the Ditrău Massif in Romania [13–16]. Studies published in "Ore Geology Reviews" (Goodenough et al., 2016) and "Lithos" (Honour et al., 2018) have established the Ditrău Massif as a major monazite mineralization deposit, containing high levels of LREE, which are considered to be critical to contemporary technology. This deposit has been identified as one of the most significant sources of REEs in Europe [7, 13]. The REE content of monazite can vary depending on the deposit, but it typically ranges between 0.1 and 10% REO (rare earth oxide). Due to the increasing demand for REEs in high-tech industries, the extraction of REEs from monazite has become an area of significant interest in recent years [10]. However, the extraction of REEs from monazite is a challenging task due to the presence of other elements and minerals. Several methods have been proposed for the extraction of REEs from monazite, including chemical and physical methods. The most promising chemical methods that have been widely studied are NaOH leaching and liquid-liquid extraction. NaOH leaching uses a solution of sodium hydroxide to dissolve REEs and separate them from other minerals. Liquid-liquid extraction, on the other hand, uses a solvent to separate REEs from other elements in the mineral. Both methods have shown promising results, but further research is needed to optimize the process and make it more efficient [2, 9, 16–19].

The focus of this study was the process of extracting rare earth elements (REEs) and thorium from monazite which involved two stages. In stage 1, monazite was treated with sodium hydroxide (NaOH) to extract thorium, uranium and REE hydroxides. In stage 2, thorium hydroxide was separated from REEs by the dissolution and use of organic solvents for extraction. The study was conducted using the monazite concentrate in the Ditrău Massif (Jolotca).

2. Materials and methods

2.1. Starting materials

The laboratory tests were done using 1 kg monazitic concentrate of JolotcaDitrău. Jolotca ore is a complex ore containing rare earths and molybdenum. From a mineralogical point of view, the ore contains the following elements: monazites = 1.2%, xenotime = 0.05%, orthites = 0.1%, molybdenum = 0.1%, pyrite = 6%, ilmenite = 2%, quartz = 17%. The technological process of the ore includes physical flotation operations for molybdenum recovery and elimination of pyrite and gravitational, electrical and magnetic separations for obtaining magnetite, ilmenite and rare earths concentrates. Following the ore processing, the following products are obtained: molybdenum concentrate (w = 0.23% and Mo recovery = 74.84%) pyrite concentrate (w = 10.52%, monazite concentrate (w = 1.06% and recovery of TR_2O_3 = 56.24%) magnetite concentrate (w = 0.94%) and ilmenite concentrate (w = 0.4% with a recovery of TiO = 45.15 %).

All the reagents were of analytical grade and supplied by MERCK (sodium hydroxide (NaOH), nitric acid (HNO_3), perchloric acid ($HClO_4$), hydrochloric acid (HCl), 2-Ethylhexyl dihydrogen phosphate (HDEHP), kerosene, ammonium hydroxide (NH_4OH).

All the solutions were prepared using ultrapure water (Millipore Milli-Q).

2.2. The alkaline method of obtaining the REE

The extraction of Rare Earth Elements (REEs) from monazite, a phosphate mineral with a crystalline structure that makes leaching difficult, has been the subject of numerous studies in the scientific community. The commonly used methods for REE extraction from monazite concentrates include the use of sulfuric, nitric, hydrochloric, or mixed acids. Among these methods, the use of sodium hydroxide as a leaching agent is favored in regions where sulfuric acid is unavailable due to shortages, as it is considered to be less toxic and more environmentally friendly [9, 18, 20].

Leaching with alkali is an effective method for the extraction of rare earth elements (REEs) from monazite. The process involves the dissolution of REEs from the monazite ore in an alkaline solution, typically sodium hydroxide or potassium hydroxide.

Reactions during alkaline leaching are:

$$REPO_4 + 3NaOH \rightarrow RE(OH)_3 + NaPO_4 \quad (1)$$

$$Th_3(PO_4)_4 + 12\ NaOH \rightarrow 3Th(OH)_4 + 4Na_3PO_4 \quad (2)$$

During the leaching process, the REEs are solubilized in the alkaline solution and separated from the solid phase. The leaching conditions, such as temperature, time, and concentration of the alkali, must be optimized to ensure the maximum recovery of REEs from the monazite ore [9]. The leaching reagent used in the process presented in this paper was a 50% NaOH solution.

This technology requires adequate grinding of monazite before treatment (particle size less than 45 µm), so that extraction rates above 90% can be achieved even with relatively low ores [18, 21]. In order to improve the REE recovery, a variety of leaching techniques can be employed, including pressure leaching, oxidative leaching, and/or ultrasound-assisted leaching. These techniques can enhance the dissolution of REEs and minimize the formation of unwanted by-products.

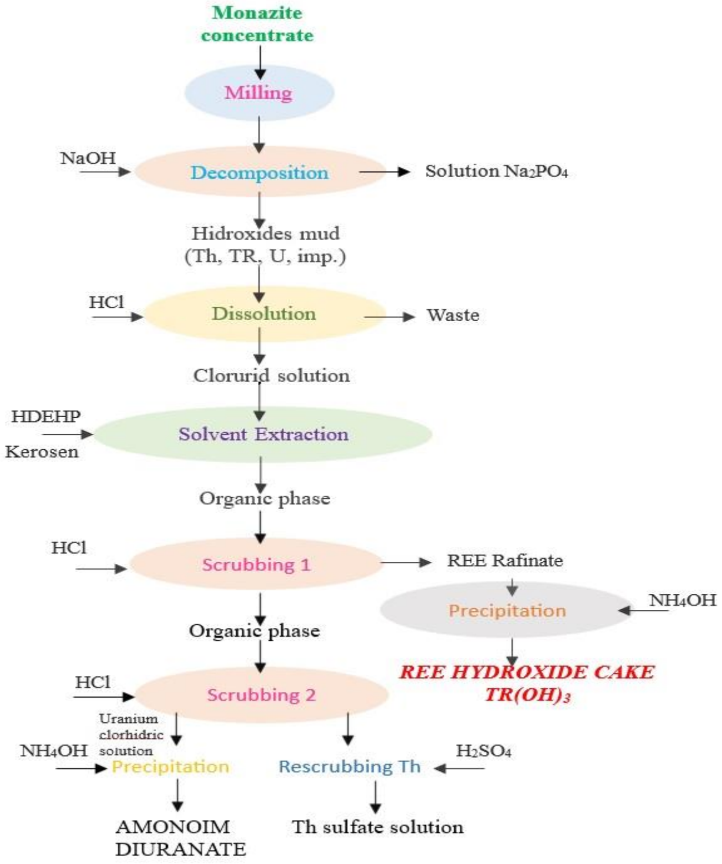

Fig. 1. Schematic representation of the monazite concentrate processing stages.

Once the REEs are in solution, they can be separated and purified through various methods, such as solvent extraction, ion exchange, or precipitation. The purified REEs can then be further processed to obtain the individual REE compounds [21].

Alkaline leaching has been demonstrated to be an effective method for the extraction of REEs from monazite ores, offering improved REE recoveries compared to conventional acid leaching methods. Furthermore, it has the potential to reduce the environmental impact associated with REE extraction compared to acid leaching processes [9, 20, 22–27].

In the present study, the factors that impact the solubilization yield of monazite were determined: particle size, sodium hydroxide concentration, reaction temperature, and reaction time. The optimal parameters for the alkaline leaching phase were established as a fine particle size (0.011 - 0.04 mm), 50% sodium hydroxide solution, a ratio of 1.5:1 sodium hydroxide to monazite, a reaction time of 2 hours, and a reaction temperature of 150°C. The results showed that the effectiveness of the alkaline leaching increases with smaller particle sizes. The reaction mixture produced was highly viscous and contained metal hydroxides, sodium phosphate, and excess of sodium hydroxide. The mixture was diluted, matured, and decanted to remove phosphate ions and excess sodium hydroxide. The reaction mixture was also washed multiple times to separate phases under optimal conditions.

The next steps consist of the hydroxy cake dissolution, extraction with organic solvents and separation of thorium and uranium from rare earths.

In order to obtain a solution containing the elements of interest, the hydroxy cake has been totally dissolved in concentrated hydrochloric acid, as presented in the following reactions:

$$Th(OH)_4 + 4HCl \rightarrow ThCl_4 + 4H_2O \quad (3)$$

$$TR(OH)_3 + 3HCl \rightarrow TRCl_3 + 3H_2O \quad (4)$$

where: TR- lanthanide hydroxides cake

The extraction of valuable elements was achieved through the addition of hydrochloric acid (HCl) 34% to a decanted suspension. The reaction conditions were maintained at 60°C for a period of 1 hour, with a consumption of 2.3L of HCl per 1 kg of monazite. The resulting solution was characterized by a final free acidity of 3.5 N. In order to achieve phase separation, the hydrochloric solution underwent a maturation process at 80°C for 2 hours, followed by decantation of the residue for 90 minutes. Subsequently, the solution was subjected to repulping with 3.5 N HCl at a 1:0.2 S:L ratio, with temperature maintained between 70-80°C. The washing solution was then combined with the initial hydrochloric solution and underwent a control filtration process to yield the final product.

Next, liquid-liquid extraction method was used in order to separate thorium from REE. The extracting solvent used and who showed high selectivity for Th (IV) was HDEHP in kerosene. The separation was based on the reaction mechanism presented below:

$$ThCl_n^{(4-n)+} + (4-n)\ (HDEHP)_2 \leftrightarrow ThCl_n(HDEHP)_{4-n} + (4-n)H^+ \quad (5)$$

where: $n=1, 2, 3, 4$

The technological parameters were as follows: 20% HDEHP extraction agent in kerosene; organic: aqueous ratio – 1:2; number of extraction steps – 6; the acidity of the aqueous phase – 3.5N HCl. For the extraction process, funnels were used for phase separation and continuous agitation was ensured using a shaker.

The refined obtained from the extraction with HDEHP is preserved for the precipitation of lanthanide hydroxides.

For the precipitation of lanthanide hydroxides, ammonium hydroxide was used and then the resulting precipitate was filtered, dried and analyzed.

2.3. Characterization methods

The laboratory experiments for extracting rare earth elements (REEs), thorium and uranium from monazite involved using specific equipment. A 4-liter reaction vessel was used for the leaching process. Other laboratory glassware such as Buchner funnel, thermostatic hob, stirrers, separation funnels, and a ball mill was used in conjunction with the reaction vessel.

The particle size analysis was performed using an Ankersmid laser particle size analyzer.

The chemical composition of the monazitic concentrate was determined using inductively coupled plasma optical emission spectrometry (Agilent 725 ICP-OES) from Agilent Technologies Inc. The analysis was performed in accordance with ASTM E 1479-99 (2011).

The uranium concentration in supernatant has been spectrophotometrically determined in presence of Arsenazo III at wavelength λ = 650 nm using a CECIL 1020 spectrophotometer for uranium-containing samples up to 2 g / L (liquid sample) or less than 0.5% (solid sample). The Volkov volumetric method was used to analyze the samples with uranium content higher than 2 g / L (liquid sample) or over 0.5% (solid sample).

3. Results and discussion

In the first part of the research the hydroxide cake was successfully obtained and the results are presented below:

3.1 Chemical analysis

Table 1 provides a comprehensive chemical analysis of the monazitic concentrate used as the basis for the conducted experiments. The results of the analysis confirmed the presence of three significant elements: Thorium (Th), Uranium (U), and Rare Earth Elements (REE). These elements are crucial due to their unique properties and various industrial applications.

Table 1

Chemical analysis for monazitic concentrate

Sample	Unit	REE [%]	Th [%]	U [%]
Monazitic concentrate	wt.%	44	2.7	0.19

3.2 Granulometric characterization of the sample

Fig. 2 shows the particle measurements which were taken in the range of 0.1-300 microns using number, length, area, and volume methods. The volume measurement method is considered the most representative, with an average particle diameter of 4.19 microns and a 97.84% confidence level. The test was conducted in a wet environment at a temperature of 200°C with a concentration of 0.05 mg/ml and 120.000 granules/ml. The measurement lasted 5 seconds with a frequency of 200 Hz and a rotation speed of 12.000 RPM. Over 95% of the material has a grain size less than 6.86 microns and the most common grain size was 4.29 microns. It is very important that the particle size is less than 45 µm, so that extraction rates above 90% can be achieved even with relatively low ores.

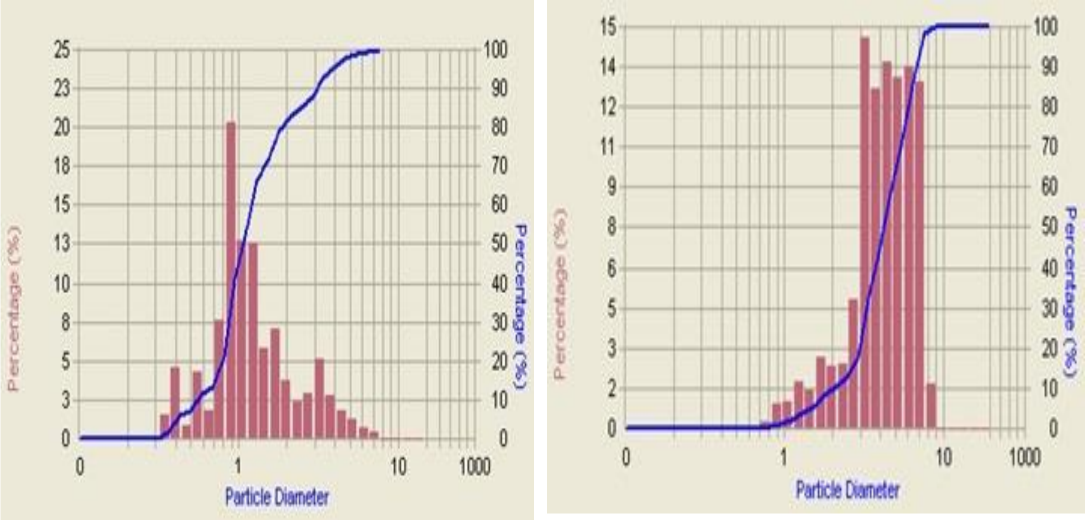

Fig. 2. Graphs of the granulometric analysis report.

The histogram shows that most of the granules (70%) are in the size range of 3-6.86 microns.

3.3 Experimental results

Fig. 3 shows the experimental data obtained on the sedimentation of the diluted and matured reaction mixture and the reaction mixture after washing.

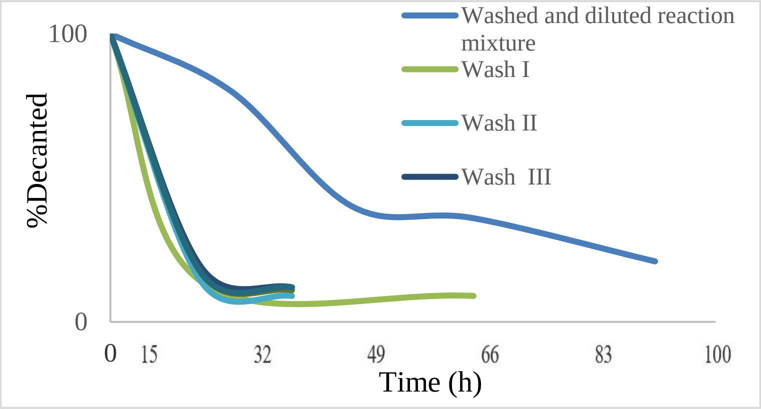

Fig. 3. Sedimentation of the resulting reaction mixtures.

Fig. 4 a) presents experimental data on the uranium content in various mixtures, including the initial monazitic concentrate, undiluted reaction mixtures, the saturated and matured reaction mixture, and the waters from the first repulping, b) presents experimental data on the rare earth content in both the initial monazitic concentrate and the hydroxide cake obtained.

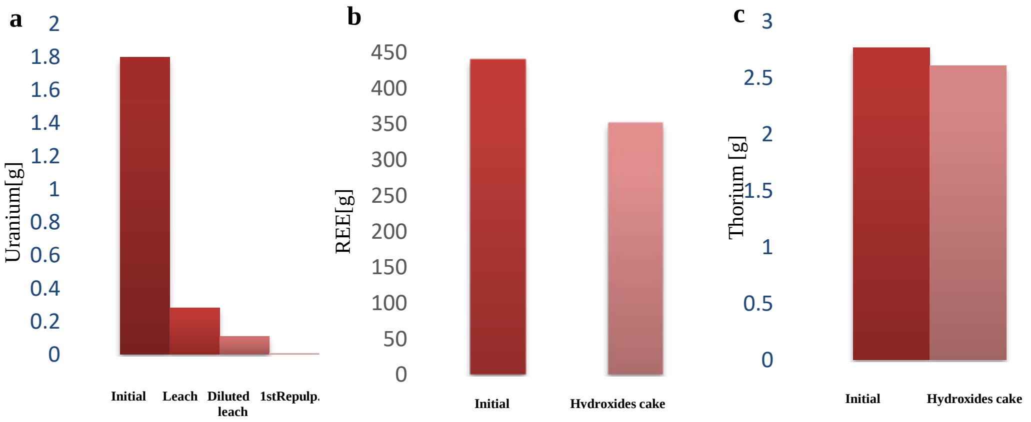

Fig. 4. a, b, c Graphs showing the U [g], Th [g], REE [g] contents in initial concentrate and hydroxides cake.

The results indicated a transition of **80%** of rare earths into hydroxide cake, c) presents experimental data on thorium content in both the initial monazitic concentrate and the hydroxide cake obtained. The results indicated a **94%** transfer of thorium into the hydroxide cake. In the second part, the dissolution of the hydroxide cake, the extraction with organic solvents and the separation of thorium from rare earths were carried out. The results are presented below. Fig. 5 and Fig. 6 present chemical composition of the hydroxide cake solution after dissolution and redissolution.

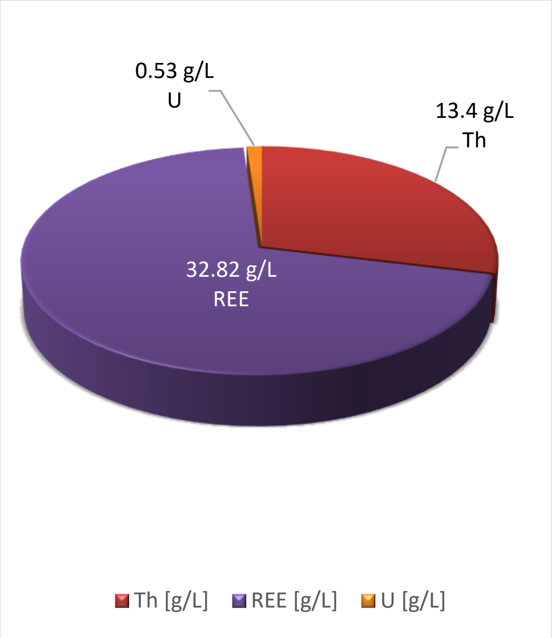

Fig. 5. The chemical composition of the solution after the first hydrochloric dissolution.

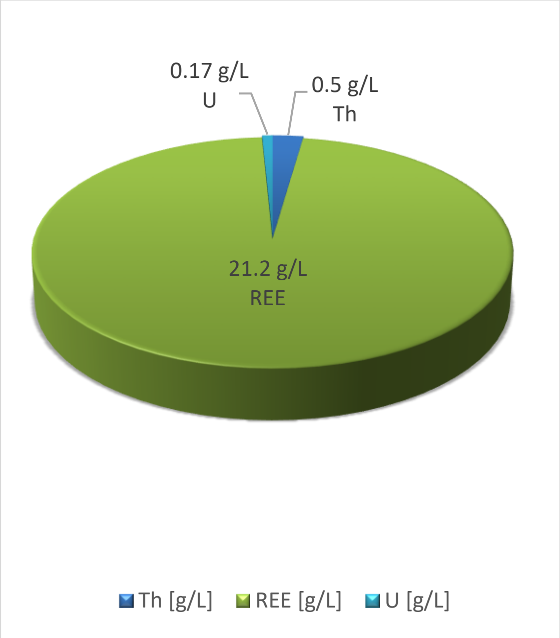

Fig. 6. The chemical composition of the solution after the second hydrochloric redissolution.

After the extraction process with organic solvent 1 L of refined was obtained. The chemical composition of the refined is presented in Table 2.

Table 2

Chemical composition of the refined solution

Sample	REE g/L	Th g/L	U (g/L)
Refined	52.83	0.38	0.60

It is noted that almost all of Th was extracted with the organic solvent. As for the contents of REE, it is found that almost all the quantity from the hydrochloric solution wash is found in refined.

The refined solution was precipitated with ammonium hydroxide and filtered. The result is shown in Fig. 7.

Fig. 7. Lanthanide hydroxides precipitate.

Table 3

Chemical composition of the precipitate

Sample	REE %	Th %	U %
Lanthanide hydroxides precipitate	30.99	<0.005	0.005

The difference in uranium content is found in the solution from filtration of the precipitation of lanthanide hydroxides.

4. Conclusion

Purified REE hydroxides were successfully extracted from monazite ore originating from Jolotca-Ditrau Romania by applying the described processes.

The total recovery efficiency for the entire process of dissolving the HCl hydroxide cake was **46.09%** for REE, and the total elimination efficiency of Th was 99.98% and of U 99.73%.

The extraction of Th from the HCl solution was performed using HDEHP/kerosene mixture as solvent. From 1 kg monazite ore, 203.8 g (46.28 %) of REE hydroxides were obtained after precipitation with ammonium hydroxide and ~0,22g Th hydroxide was retained in the organic solution.

Acknowledgments

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