

## Separation of Thorium (Th) from Monazite Sand of Bangka Island using Primene JMT Solvent Extraction Method

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Article received: 19 May 2022, revised: 19 May 2022, accepted: 30 November 2023

DOI: [10.55981/eksplorium.2023.6480](https://doi.org/10.55981/eksplorium.2023.6480)

### ABSTRACT

Thorium is an essential element as an alternative nuclear fuel to replace uranium. Thorium is found in the mineral monazite, which is a by-product of the alluvial tin mining process. Many methods have been used to extract and separate thorium from uranium and REEs from monazite, one of which is the organic solvent extraction method. In this research, the primene JMT, which is an extractant of primary amine compounds, was used in the method. The studied parameters are feed pH, JMT primene concentration, and stirring speed. The results show that the optimum conditions for Th extraction in monazite using solvent extraction method primene JMT were obtained at pH 0.5, extractant concentration of 2%, and stirring speed of 300 rpm with Th recovery of 94.05% while U and REE were not extracted.

**Keywords:** solvent extraction, thorium, monazite, primene JMT, primary amine

### INTRODUCTION

Monazite is a radioactive mineral which is a by-product of tin mining. It contains elements such as uranium (U), thorium (Th), rare earth element (REE), and phosphate (PO<sub>4</sub>) [1]. Rare earth metals are often found in the by-product minerals in tin mining such as monazite and xenotime on the islands of Bangka and Belitung [2]. There are at least 12 rare earth metal oxides identified from tin mining results in the Bangka Belitung Islands Province. Minerals that have economic value are ilmenite (32.43%), zircon (16.65%), cassiterite (12.59%) and monazite (11.76%) [2].

Thorium can be used as an alternative nuclear fuel to replace U. Th is an alternative to nuclear fuel because of its abundance in nature [3]. Indonesia is estimated to have

thorium reserves of 130,974 tons spread across several regions, such as Singkep Island, Bangka Belitung, West Kalimantan, and Mamuju [4].

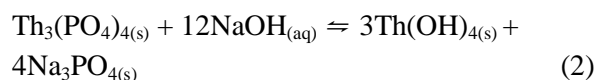
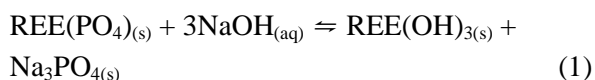
Separation of U from Th in monazite has been carried out by the solvent extraction method [5], the precipitation method [6], and solvent solvent-impregnated resin method [7]. In the solvent extraction method, the extractant used is trioctylamine (TOA) which has the trade name alamine. From this method, U is extracted 100%, but the purity is still below 70%, as there is 32.44% Th [5]. With the precipitation method, Th separation from monazite uses sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrochloric acid (HCl) reagents. This method produces a Th purity of 73.02% and 78.73%, respectively, with U still included at 18.26% and 25.03% [6]. The solvent-

impregnated resin method has extracted 81.13% Th, 25.15% U, and 0.09% REE, so the purity of Th was still low [7].

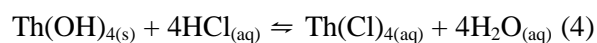
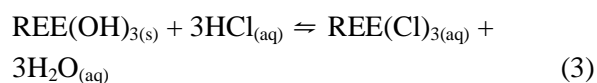
The results obtained from those previous research were not yet optimal as the U and Th have not entirely separated. Therefore, in this research, thorium will be separated from monazite using a solvent extraction method with primene JMT (tri-alkyl-methylamine). The solvent extraction method is used to separate compounds based on their solubility. This method has many advantages, including simplicity of process, time, equipment, and selectivity for the desired element [5]. The primene JMT, which is a group of primary amines, is the most selective for extracting thorium [8]. This research aims to obtain optimum conditions for Th extraction using the solvent extraction method using primene JMT. The parameters studied were the effect of solvent pH, solvent concentration, and stirring speed on Th recovery.

## THEORY

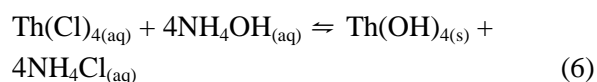
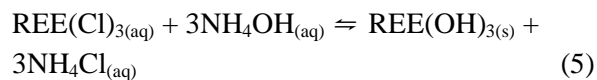
Monazite sand processing is carried out by alkaline decomposition using NaOH. The preparation begins by grinding the monazite sand to reduce the particle size. NaOH is used to reduce the amount of phosphate, which can interfere with the process of separating elements in monazite sand. During the decomposition process, REE phosphate in monazite will be converted into REE hydroxide, which is easily soluble in acid and can be precipitated as sodium phosphate. The result of the decomposition of monazite sand is residue (U, Th, REE)OH<sub>3</sub> [9]. The reaction between REE(PO)<sub>4</sub> and Th<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub> with NaOH is as follows [9]:



The resulting residue will be processed for selective/partial dissolution using HCl with a pH of 3.7. This process's objective is to dissolve REEs in the residue as much as possible while the radioactive elements (U and Th) are dissolved as little as possible. The reaction between REE(OH)<sub>3</sub> dan Th(OH)<sub>4</sub> with HCl is as follows [10]:



After obtaining the chloride solution, precipitation is carried out to precipitate radioactive elements in the form of uranium and thorium using NH<sub>4</sub>OH, and the precipitate will be used for the total dissolution process to make the feed solution. The reaction between REE(Cl)<sub>3</sub> dan Th(Cl)<sub>4</sub> with NH<sub>4</sub>OH is as follows [11]:



The feed solution is made using the acid method by adding concentrated sulfuric acid to the (Th, REE) hydroxide precipitate in a ratio of 1:1, then heating it to 210°C for 1 hour to produce thorium sulfate Th(SO<sub>4</sub>)<sub>3</sub><sup>2-</sup>. If the temperature is more than 210°C, thorium pyrophosphate will form, which is difficult to dissolve, and the viscosity of the feed solution increases, making it difficult for the following extraction process [8]. The higher the temperature will increase the reaction rate between sulfuric acid and the (U, Th, REE) hydroxide precipitate [9].

The added sulfuric acid aims to dissolve the U, Th, and REE elements so that they can bind with the sulfate ion. Thorium is easier to extract with primary amines, while uranium is easier to extract with tertiary amines. The use of more and more concentrated sulfuric acid produces a greater number of H<sup>+</sup> ions, increasing proton attack activity. The dissolved uranium and thorium become U<sup>4+</sup> and Th<sup>4+</sup> ions. These ions will bind the SO<sub>4</sub><sup>2-</sup> compound in sulfuric acid. The reaction between U<sup>4+</sup> dan Th<sup>4+</sup> with SO<sub>4</sub><sup>2-</sup> is as follows [5]:



Kerosene is used as an organic solvent because it has a low level of toxicity and is cheap and easy to obtain. The solvent helps control extraction, reducing viscosity and hydrophilic properties, thereby facilitating complex formation with thorium [12]. The addition of 1-decanol reduces the third phase, which continues to increase according to conditions with higher pH values because long-chain alcohols can increase the phase separation rate and clarity of the organic phase [13].

Extraction of metals by amines depends on the capacity of metal ions to form anionic or neutral species in the aqueous phase. This species is extracted using an anion exchange mechanism. Primary amine anions are preferred for thorium extraction in sulfate solutions because their structure is simpler than tertiary amines, which are more bulky and more difficult to bind to thorium [8].

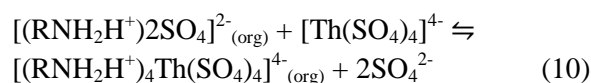
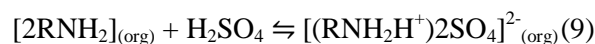
Primene JMT (tri-alkyl-methylamine) is used as a liquid extractant, which can increase thorium binding. The extractant concentration affects the ability of the solvent to extract elements from the water phase. The primary

amine in Primene JMT has a positive inductive effect that increases the electron density of the N atom [14].



Figure 1. Primene JMT structure [14].

Stirring the solution increases the speed of the reaction by allowing more collisions between particles. The stirring speed affects how well the particles are distributed between the water phase and the organic phase [15]. Appropriate speeds are required to minimize the risk of emulsion formation, where the organic phase and the aqueous phase mix.



The reaction above can be explained by the fact that the active site in the primene JMT solvent interacts with the H<sup>+</sup> ion in H<sub>2</sub>SO<sub>4</sub> to produce a complex [(RNH<sub>2</sub>H<sup>+</sup>)<sub>2</sub>SO<sub>4</sub>]<sup>2-</sup> in the organic phase. The complex then interacts with the thorium sulfate complex anion [Th(SO<sub>4</sub>)<sub>4</sub>]<sup>4-</sup> to produce the complex [(RNH<sub>2</sub>H<sup>+</sup>)<sub>4</sub>Th(SO<sub>4</sub>)<sub>4</sub>]<sup>4-</sup> and releases the SO<sub>4</sub><sup>2-</sup> ion [16]. This process explains that the thorium element can bind to the active amine site in primene JMT.

The extraction results obtained from the analysis are used to calculate the recovery percentage with the following equation:

$$\%R = \frac{M_{feed} - M_{raffinate}}{M_{feed}} \times 100\% \quad (11)$$

The value of M<sub>raffinate</sub> is the mass of elements in the raffinate or aqueous phase, and M<sub>feed</sub> is the mass of elements in the feed solution.

## METHODOLOGY

The materials used in this research were Bangka monazite sand, primene JMT (tri-alkyl-methylamine),  $C_{10}H_{22}O$  (1-decanol),  $C_{15}H_{32}$  (kerosene),  $H_2SO_4$  (sulfuric acid),  $NH_4OH$  (ammonia),  $NaOH$  (sodium hydroxide) and  $HCl$  (hydrochloric acid).

The tools used in this research were beakers, hot plates, measuring cups, filter paper, separating funnels, stirring rods, magnetite stirrers, pH meters, vacuum filters and stopwatches. The instrumentation used is Shimadzu UV-2600 UV-Vis Spectrophotometry and Perkin Elmer Optima 8300 Inductively Coupled Plasma Optic Emission Spectrometry (ICP-OES).

Monazite was prepared by crushing and filtering using 325 mesh, then alkaline decomposition at  $140^\circ C$  for 4 hours. After decomposition, the residue obtained was dissolved using  $HCl$  at pH 3.7 and filtration to separate the  $REE(Cl)_3$  solution from the uranium, thorium and REE hydroxide precipitate. The (U, Th, LTJ) $OH_3$  precipitate was dissolved with  $NH_4OH$  and used to prepare the feed solution.

The feed solution was made from 500 grams of uranium, thorium and REE hydroxide precipitate that was added with 500 mL of concentrated  $H_2SO_4$ , was heated to  $210^\circ C$ , and stirred for 1 hour. Then, 1000 mL of water was added, stirred for 15 minutes, and filtered to obtain the feed solution. This feed solution was analyzed using a UV-Vis Spectrophotometer, ICP-OES, and gravimetry which has gone through a method validation process. The equipment for creating the feed solution can be seen in Figure 2.

The extractant consisted of 12% primene JMT (tri-alkyl-methylamine), 6% 1-decanol and 82% kerosene. The feed solution and extractant were mixed in a 1:1 ratio, stirred for 5 minutes, then separated into an organic

phase and an aqueous phase using a separating funnel. The aqueous phase was analyzed for concentrations of U, Th, total REEs and impurities (Al, Mg, Zn, Fe and Ca) using a UV-Vis spectrophotometer, ICP-OES and gravimetry. This process was done repeatedly with variations in pH 0, 0.5, 1, 1.5, and 2. The highest pH used was pH 2 because, according to [17], at a pH above 2, the extracted Th decreases



Figure 2. Process equipment for making feed solution.

The feed solution pH 0.5 was used as the aqueous phase (A), while the extractant consisted of primene JMT in kerosene with varying concentrations (2%, 4%, 6%, 8%, 10%) as the organic phase (O). A and O were mixed in a 1:1 ratio, stirred for 5 minutes, and separated using a separating funnel. Then, A was analyzed for concentrations of U, Th, total REEs and impurities (Al, Mg, Zn, Fe and Ca) using a UV-Vis Spectrophotometer, ICP-OES and Gravimetry.

The feed solution pH 0.5 as aqueous phase (A) and 2% primene JMT extractant in kerosene as organic phase (O) were mixed in

a 1:1 ratio. The stirring was carried out at various speeds (100, 200, 300, 400 and 500 rpm), for 5 minutes, then the organic phase and aqueous phase were separated using a separating funnel. The aqueous phase was analyzed for concentrations of U, Th, Total REEs and impurities (Al, Mg, Zn, Fe and Ca) using a UV-Vis Spectrophotometer, ICP-OES and Gravimetry.



Figure 3. Process of separating the organic phase and aqueous phase.

## RESULTS AND DISCUSSION

### Effect of Feed pH

The extraction recovery with variations in pH is presented in Figure 4. It can be seen that the higher the pH, the greater the Th, U, and REE extracted. The decrease in Th recovery is due to the higher pH, Th will begin to precipitate. The presence of Th, which begins to precipitate at a higher pH, causes the presence of dissolved thorium to decrease so that the Th extracted becomes smaller.

Apart from that, it can also be seen that U and REE are still being extracted, and the

recovery is higher at a higher pH. From the data above, the optimum pH for Th extraction was chosen at pH 0.5 with Th, U, and REE extraction recoveries of 90.55%, 32.94% and 46.31%, respectively.

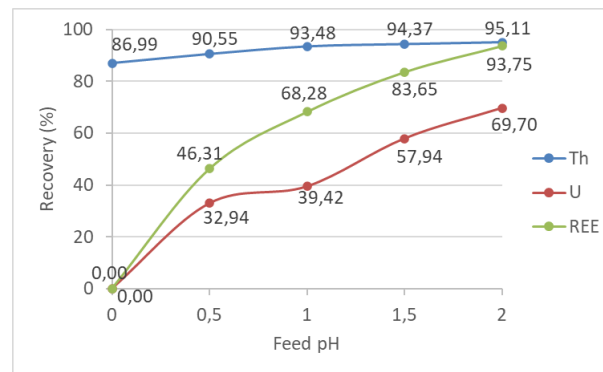


Figure 4. Extraction recovery of feed pH variations

### Effect of Primene JMT Concentration

The extraction recovery with variations in JMT primene concentration is presented in Figure 5. The higher the concentration of primene JMT, the extraction recovery of Th, U, and REE also increases (Figure 5). The extractant concentration has a direct effect on the extraction process because the capacity of the extractant increases with increasing extractant concentration so that it can bind more elements. This phenomenon is in line with research [5], where U extraction recovery increased when the concentration of trioctylamine as an extractant also increased.

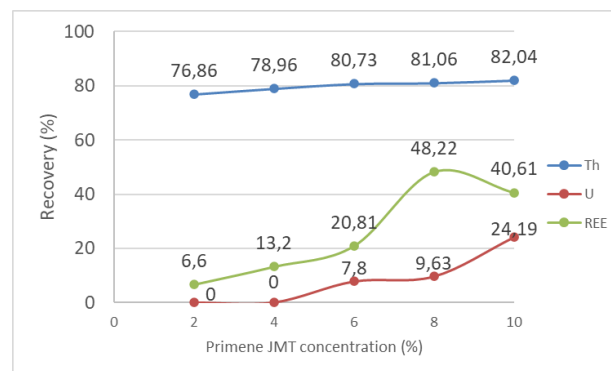


Figure 5. Extraction recovery of Primene JMT concentration variation

From the extraction recovery results, a 2% JMT primene concentration was chosen as the optimum concentration because it gave a fairly high Th extraction recovery percentage, namely 76.86%. In contrast, the relatively little (6.60%) REE was extracted, while U was not extracted.

### Effect of Stirring Speed

The optimum concentration for thorium extraction with JMT primene is 2%, and the optimum pH is pH 0.5. Thorium extraction was carried out by varying the stirring speed (100, 200, 300, 400, 500 rpm) to achieve higher extraction recovery.

It can be seen that Th extraction recovery increases quite well from a stirring speed of 100 rpm to 200 rpm, namely 80.60% to 93.06% (Figure 6). However, from 200 rpm to 500 rpm, Th extraction recovery tends to be constant, or the increase is not very significant. The stirring process will increase contact between the JMT primene extractant and the elements in the feed solution so that Th extraction recovery increases when the stirring speed increases from 100 rpm to 200 rpm. The extraction recovery Th tends to be constant when the stirring speed is increased from 300 rpm to 500 rpm because the extraction process has reached an equilibrium state [18]. This phenomenon was also seen in research on the extraction of cerium (Ce) with HCl, where Ce recovery increased from 55.43% to 75.16% when the stirring speed increased from 100 rpm to 200 rpm and tended to remain constant until it fell to 64.51% when the stirring speed increases from 300 rpm to 400 rpm [15].

Meanwhile, U and REE tend not to be extracted at a stirring speed of 100 rpm to 400 rpm and are only extracted at 3.33% and 5.84% at a rotational speed of 500 rpm. From these results, a stirring speed of 300 rpm was

chosen as the optimum stirring speed where Th extraction recovery reached 94.05%, while U and REE were not extracted.

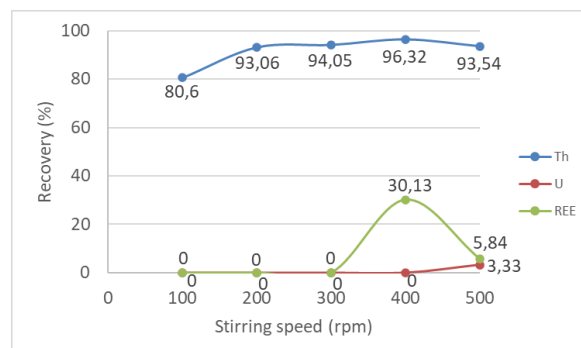


Figure 6. Extraction recovery of stirring speed variation.

### CONCLUSION

Based on the results of research and data analysis, the optimum conditions for Th extraction in monazite using the solvent extraction method primene JMT were obtained at pH 0.5, extractant concentration of 2%, and stirring speed of 300 rpm with Th recovery of 94.05%. At the same time, U and REE were not extracted. It is thought that Th recovery can still be increased by increasing the extraction time, which will be carried out in the subsequent study.

### ACKNOWLEDGMENT

The author would like to thank colleagues at the Centre for Nuclear Minerals Technology-BATAN (PTBGN-BATAN) for providing materials and facilities during the author's research.

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