Solvent extraction of Thorium from Malaysian xenotime using Tributyl Phosphate (TBP)

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Abstract. Growing interest in environmental concern and vast industrial application makes Thorium popular and widely studies nowadays. In this study, solvent extraction process was done to determine the optimized parameters for the extraction of thorium. Parameters studied are the concentrations (M) of nitric acid (HNO3), percent (%) of Tri-Butyl Phosphate (TBP) in diluent and the volume ratio of acid to organic phase (VA:VO). The mixed rare earth (RE) oxalate powder was dissolved in HNO3 and Thorium elements was extracted using TBP diluted in kerosene. Energy dispersive x-ray fluorescence (ED-XRF) instrument was used to analyze the initial and final concentration of Thorium left in the aqueous solution. From the ED-XRF quantitative values, calculations were made to determine the extraction efficiency of Thorium. In the end of experiment, it is found that the optimized parameters are at 7M HNO3, 20% TBP diluted in kerosene and at VA:VO ratio of 2:3.

1. Introduction
Xenotime, bastnaesite and monazite are among minerals that contains rare elements and radioactive elements such as Thorium and Uranium. Due to the significant amount of rare earth in these minerals, it makes them an important source of RE. In Malaysia, xenotime and bastnaesite mineral was obtained from tin mining industrial by product and higher in heavy RE content in comparison to monazite [1]. Xenotime have high content of Yttrium aside of heavy RE elements from Lanthanide group which makes it termed YPO4. Economic value of Yttrium, Gadolinium, Dysprosium, Erbium and other REE in the mineral is rather high in demand due to their unique catalytic, chemical, electrical, magnetic and optical properties [16]. These heavy RE contents in xenotime can be separated further after recovery of thorium from the mineral ass a spin-off.

As an alternative in replacing Uranium as fuel for nuclear power plant, Thorium element become popular and widely studies nowadays. Various technique was done to recover Thorium, Uranium and REE from various sources such as ion-exchange, selective precipitation, chromatography, electrophoresis and liquid-liquid extraction methods [2]. Liquid-liquid extraction is the technology initially developed to recover Uranium from ore-leach liquor [6]. The method used was then adapted for recovery of other REE including Thorium. Studies in separation of Thorium from various sources was made possible via some technique including solvent extraction, direct precipitation and ion exchange [14]. The purification of thorium was made by repeated transfers between organic and aqueous medium.
Compared to direct precipitation and ion exchange, solvent extraction technique is more eminent due to its speed, large throughput and non-complicated procedure [12].

According to Gupta et al. [5], popular alkylphosphorus extractant used for separation of uranium and thorium includes TBP, Di-2-Ethylhexylphosphoric acid (DEHPA) and Tri-N-Octylphosphine Oxide (TOPO). Tributyl Phosphate (TBP) is a type of organophosphorus extractant which is prominent in nuclear industries in the recovery of Uranium and Thorium from rare earth minerals [8]. Since TBP is less flammable and more stable makes it preferable during the World War II to separate Uranium [15]. Various studies are done to improve the extraction ability of each extractant. Previous studies done via TBP solvent to extract various types of elements such as Molybdenum [4], and Cerium(IV) [3] from nitric acid media. TBP have low vapor pressure which makes it safer for handling and storing with reduced flame risk [13]. Researchers studied different parameters and media to improve the extraction efficiency of TBP.

Famous use of TBP in extraction were done mainly for the recovery of Uranium since it is highly selective to uranium [13]. In this study, the solvent extraction via TBP in kerosene was chosen to recover Thorium instead. Separation of Uranium from Thorium via extraction is somewhat difficult to achieved because of the limited variance oxidation states which thorium poses [9]. However, for this study, Malaysian xenotime undergone cracking, leaching, selective precipitation and decomposition process prior in obtaining mixed RE and Thorium oxides powder which no longer contains Uranium. Figure 1 shows the composition of Thorium and other RE oxides composition elements after alkaline fusion. This mixed oxides will further undergo extraction process for recovery and purification of thorium.

![Figure 1. Composition in percent of mixed rare earth and thorium oxides after alkaline fusion.](image)

The paper will be focusing on optimized extraction parameters which include molarity of HNO₃, percentage of TBP in the diluent and the ratio of acid to organic Vₐ:Vₒ. Single stage extraction will be done and analyze under ED-XRF to determine the concentration (ppm) before and after extraction process.

2. Experimental
The extraction process was done by mixing aqueous solution with extractant and allows extraction to take place. RE mixed Thorium Oxalate was processed in prior through alkaline fusion technique [7]. The xenotime mineral fused with sodium hydroxide in a furnace, washed with distilled water to remove loose phosphate content and further leached with concentrated at with heating. Final form of oxalate was precipitated from the acidic solution using oxalic acid. The oxalate undergo decomposition into oxide form and analyzed under ED-XRF for the determination of thorium content. The analysis was done using Thermo Scientific ED-XRF model ARL Quant ED-XRF Analyzer.

Initial steps for the solvent extraction procedure are the preparation of aqueous and organic phase. Aqueous solutions were made by dissolving oxalate powder with HNO₃. Then, extractants were prepared by mixing TBP in kerosene as the diluents. Extraction process was the done by mixing both
liquids with 30 minutes of vigorous stirring using magnetic stirrer in a beaker at room temperature (25 ± 2°C). The two-layer solution was transferred into a separatory funnel and waited until appeared clearer and transparent before flush out into two different sample bottle. The flow chart in Figure 2 shows the overall process of solvent extraction. This experiment has three different batch of solvent extraction process done.

![Flow chart of solvent extraction process](image)

**Figure 2.** The overall process of solvent extraction.

The analysis to determine Thorium concentration was done via ED-XRF for initially prepared aqueous solution and the aqueous solution after undergone solvent extraction. The extraction efficiency (E) was determined from Equation (1):

\[
E(\%) = \frac{C_{\text{Th, initial}} - C_{\text{Th, final}}}{C_{\text{Th, initial}}} \times 100\%
\]  

(1)

where,

\( C_{\text{Th, initial}} \) = Concentration of thorium in initial aqueous solution before extraction and,

\( C_{\text{Th, final}} \) = Concentration of thorium in final aqueous solution after extraction.

The first batch extraction’s parameter study was done to determine the effect of different HNO\(_3\) concentration toward the efficiency of solvent extraction process. Five different molarity used were 1, 3, 5, 7 and 9M HNO\(_3\). The concentration of TBP in kerosene was set at 20% whilst the ratio of \( V_A : V_O \) was kept at 1:1.

Second batch extraction was done to determine optimum percentage of TBP in kerosene during extractant preparation. Six different organics prepared which are at 5%, 10% 15%, 20%, 25% and 30% TBP in kerosene. Molarity of HNO\(_3\) selected based on optimum extraction efficiency value from the first batch extraction. Fixed variables in this process is the amount of oxalates (0.5 gram) and \( V_A : V_O \) of 1:1.

Third batch extraction was done to determine the optimum \( V_A : V_O \) ratio. The variation ratio was made at six different ratios of 1:3, 1:2, 2:3, 1:1, 3:2 and 2:1. The optimum percentage of TBP in the diluent and optimum molarity of HNO\(_3\) from previous experiment was used while keeping the mixed oxalate at 0.5g.
3. Results and discussion

3.1. Optimization of HNO₃ concentrations towards extraction
Tabulated data in Table 1 for first parameters studied showed that a single stage extraction give efficiency of Thorium at 28.23% when 1 M HNO₃ used. After increased the concentration to 3 M and 5 M, the efficiencies become 72.39 and 82.12% respectively. Studies on 7 M HNO₃ shows significant extraction efficiency with 83.13% then dropped to 74.75% for 9 M HNO₃. The $C_{Th, initial}$ and $C_{Th, final}$ were shown in Table 1.

| Molarity of HNO₃ | Concentration (ppm) | E (%) |
|-----------------|---------------------|-------|
|                 | $C_{Th, initial}$   | $C_{Th, final}$ |       |
| 1M              | 56.50               | 40.55   | 28.23 |
| 3M              | 52.70               | 14.55   | 72.39 |
| 5M              | 45.30               | 8.10    | 82.12 |
| 7M              | 40.90               | 6.90    | 83.13 |
| 9M              | 44.15               | 11.15   | 74.75 |

Table 1. ED-XRF results of aqueous solution before and after extraction of Thorium using different concentration of HNO₃.

Figure 3 shows the plotted E (%) against concentration of HNO₃ for molarity study. The graph indicates that efficiency improved when molarity of HNO₃ increases. The increment was highest at 7 M HNO₃. After increased to 9 M, extraction efficiency shows a significant drop. The increasing efficiency of thorium (1 M to 7 M HNO₃) might resulted a higher distribution coefficient between aqueous and organic phase [11]. However, at higher concentration of acid, the extraction mechanism might change to solvation instead of cationic exchange due to formation of neutral complex with nitrate anions [10].

3.2. Optimization of TBP concentration in kerosene towards extraction
Second extraction parameter study was done using different percentage of TBP in kerosene. From Table 2, the value of extraction efficiency is 33.22% when 5% of TBP in kerosene was used. The efficiency
become 73.73% when 10% TBP added and further increased to 91.78 for 15% TBP. The extraction efficiency lingered around 98.78, 97.62 and 94.84% when 20, 25 and 30% TBP in kerosene was introduced respectively.

**Table 2.** ED-XRF results of aqueous solution before and after recovery of thorium using different concentration of TBP in kerosene.

| Percent of TBP in kerosene | Concentration (ppm) | E (%) |
|----------------------------|---------------------|-------|
|                            | C_Th, initial       | C_Th, final |       |
| 5%                         | 45.15               | 30.15   | 33.22 |
| 10%                        | 42.45               | 11.15   | 73.73 |
| 15%                        | 48.05               | 3.95    | 91.78 |
| 20%                        | 40.90               | 0.50    | 98.78 |
| 25%                        | 39.85               | 0.95    | 97.62 |
| 30%                        | 42.60               | 2.20    | 94.84 |

Figure 4 shows the graph of extraction efficiency against percentage of TBP in the extractant. The graph showed an increment when more TBP is used for extraction of Thorium. Start from 5% until 20% TBP. However, the efficiency starts to decreased slightly when more TBP used. This might due to the increasing viscosity of extractant which affect the diffusion rate of Thorium between the two phases [11] Thus, the significant efficiency of Thorium extraction was achieved at 20% TBP.

Figure 4. Effect of TBP concentration (%) in kerosene towards extraction efficiency of thorium.

3.3. Optimization of aqueous solution to extractant ratio towards extraction

The third parameter study is about the volumetric ratio of aqueous solution containing the Thorium (V_A) with the organic extractant (V_O). Six different ratio (V_A:V_O) was used, 1:3, 1:2, 2:3, 1:1, 3:2 and 2:1 From data in Table 3, the extraction efficiency relatively high for V_A:V_O of 1:3, 1:2 and 2:3 which is 93.21, 91.18 and 94.75 % respectively. When more aqueous added such as 1:1, 3:2 and 2:1, the efficiency dropped significantly from 83.13 to 72.96 until 58.70 %.
Table 3. ED-XRF results of Thorium in aqueous solution before and after extraction at different volumetric ratio of aqueous solution to extractant (V_A:V_O).

| Ratio of acid to organic (V_A:V_O) | Concentration (ppm) | E (%) |
|-----------------------------------|---------------------|-------|
|                                   | C_{Th, initial} | C_{Th, final} |
| 1:3                               | 44.20            | 3.00    | 93.21 |
| 1:2                               | 44.80            | 3.95    | 91.18 |
| 2:3                               | 38.10            | 2.00    | 94.75 |
| 1:1                               | 40.90            | 6.90    | 83.13 |
| 3:2                               | 43.45            | 11.75   | 72.96 |
| 2:1                               | 39.95            | 16.50   | 58.70 |

From Figure 5, the graph shows linear pattern for when 1:3, 1:2 and 2:3 ratio used. After that, the extraction efficiency dropped linearly when 1:1, 3:2 and 2:1 ratio was used. It can be concluded from the graph, when volume of aqueous solution is more than volume of extractant (2:3 until 2:1), the ability of TBP to extract thorium become less efficient.

Figure 5. Effect of different volume of acid to organic phase (V_A:V_O) towards thorium extraction efficiency.

4. Conclusion
The optimization of solvent extraction technique focusing on Thorium from crude oxalate products of xenotime via alkaline fusion was achieved. From the experiments, the optimum acid concentration was at 7 M HNO_3 with extraction efficiency of 83.13 %. In the other hand, optimum 20 % of TBP content in the kerosene resulted in best efficiency with 98.78 % thorium recovered. Lastly, the optimum volume ratio between aqueous solution and extractant used is at 2:3 (V_A:V_O) with recovery percent of 94.75 %. Further study can be done by using different parameters and also by doing scrubbing to removed several elements prior to stripping process in order to increase the Thorium stripping efficiency. The extracted Thorium Oxalate from loaded organic will be further studied through precipitation technique in order to achieve Thorium of higher purity.
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