RECENT DEVELOPMENT ON RECOVERY OF URANIUM, THORIUM AND RARE EARTHS FROM MONAZITE BEACH SAND OF INDIA

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ABSTRACT
Separation of U(VI) and Th(IV) from a number of other metal ions present in monazite leach solution has been investigated using tris(2-ethylhexyl) phosphate (TEHP) and tri-isoo amyl phosphate (TiAP) dissolved in n-paraffin under varying experimental conditions such as nature of diluents, nitric acid, extractant and metal ion concentration and nature of strippants etc. Based on these studies, selective recovery of U(VI) from real monazite leach solution (HNO₃ medium) has been carried out using counter current extraction mode employing 0.1 M TEHP/n-paraffin as solvent. The recovery of Th(IV) from raffinate solution was done using 5 stages counter current extraction mode employing 1 M TiAP/n-paraffin as solvent.

Keywords: Thorium, Uranium, Monazite, Solvent Extraction, Counter-Current

INTRODUCTION
In a developing country like India there is always an increasing demand of nuclear power to sustain its social, industrial and economic growth. Indian nuclear energy programme consists of three stages, staring from construction of Pressurized Heavy Water Reactor (PHWR) with the help of natural uranium as a nuclear fuel and heavy water as moderator under high pressure and production of 239Pu. The second stage consists of the construction of fast reactor containing natural uranium-plutonium as fuel material and thorium oxide as blanket. In the last stage, there will be enough 233U for construction of Advanced Heavy Water Reactor (AHWR) or Boiling Water Reactor (BWR) which will help the generation of electricity from existing nuclear fuel [1]. For generation of enough 239Pu for second stage, India needs a constant supply of natural uranium which will come from various resources including secondary resources such as phosphoric acid and monazite sand as India has a limited reserve of primary source of uranium [2]. However, India has a vast deposit of monazite as beach sand containing 10 % ThO₂, 60% rare earths (RE) and 0.38 % U₃O₈ and hence considered as a secondary source of uranium [3-4]. Monazite consist of arsenate, phosphate and silicate having general chemical formula ABO₄, where A indicates RE, U, Th, Ca, Bi etc. and B indicates As⁵⁺, P⁵⁺ or Si⁴⁺[5]. The processing of monazite sand is carried out through two chemical treatment routes such as 1) the digestion with hot H₂SO₄ solution and 2) the fusion with hot sodium hydroxide solution [6-10]. The second process consists of chemical attacking of monazite sand with hot, concentrated NaOH at elevated temperature where U, Th are separated as hydroxide precipitate at pH~3 [11]. The solid mass containing U, Th and RE hydroxides is called thorium cake. The separation of U, Th and RE was carried out by solvent extraction using Alamine 336 (trialkyl amine, C₈-C₁₀) and 2-ethyl hexyl phosphonic acid 2-ethyl hexyl monoester (PC88A) as extractants from chloride medium. The major drawbacks of the existing amine process are the crude and red oil formation, third phase formation, absence of suitable strippant and less uranium loading capacity of the solvent during extraction [3-4]. In the present study, a new process has been developed for selective recovery of U, Th, and REEs from monazite leach solution in nitric acid medium using counter current solvent extraction route.

EXPERIMENTAL
Materials
TEHP (E-Merck, >97 % pure), TBP (B.D.H, 97% pure), TiAP (Heavy water plant, India, 95% pure) were used without further purification. All other reagents used were of A.R grade. Stock solutions of TEHP, TBP and TiAP were prepared by diluting with n-paraffin (unless stated otherwise). The stock solution of
uranyl nitrate was prepared by dissolving pure U\textsubscript{3}O\textsubscript{8} (procured from Uranium Extraction Division, BARC) in nitric acid medium. The stock solution of thorium nitrate was prepared by dissolving thorium nitrate salt (procured from I.R.E). Unicam UV 500 (UV-visible) and Jobin Yvon Emission, Model No JY 328 (ICP-AES) machines were used to determine the concentrations of uranium and other trace metal ions in different samples during these studies.

**Leaching of thorium cake in HNO\textsubscript{3} medium**

The thorium cake collected from IRE Ltd, was dissolved in HNO\textsubscript{3} medium in presence of trace amount of aqueous HF. The dissolution was carried out in Teflon beaker at boiling for a period of 8 hours. After dissolution of thorium cake, the un-dissolved solid was separated by filtration and it was observed that ~37 % thorium cake remain un-dissolved which is well match with the un-dissolved thorium cake in HCl medium reported by IRE Ltd. The free acidity of the feed solution was adjusted to 2 M HNO\textsubscript{3} by adding adequate amount of HNO\textsubscript{3}. Similarly, the U(VI), Th(IV) and REEs concentration were adjusted by adding distilled water. Table 1 shows the results of leaching of thorium cake in different concentration of HNO\textsubscript{3} medium.

**Table 1:** Leaching of thorium cake in HNO\textsubscript{3} medium; amount of thorium cake ~7 g; amount of HF: 5 mL (0.3 % v/v of 48 % HF); leaching time ~8 hour

<table>
<thead>
<tr>
<th>HNO\textsubscript{3}, mL</th>
<th>% Un-dissolved</th>
<th>% U leached</th>
<th>% Th leached</th>
<th>% REEs leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>36.38</td>
<td>0.93</td>
<td>21.91</td>
<td>15.78</td>
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<tr>
<td>20</td>
<td>39.55</td>
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<td>25</td>
<td>39.1</td>
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<td>20.78</td>
<td>16.89</td>
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<td>37.86</td>
<td>1.02</td>
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<td>16.23</td>
</tr>
<tr>
<td>35</td>
<td>37.49</td>
<td>0.96</td>
<td>22.37</td>
<td>16.35</td>
</tr>
<tr>
<td>40</td>
<td>37.63</td>
<td>0.88</td>
<td>21.48</td>
<td>16.68</td>
</tr>
</tbody>
</table>

**Extraction experiments**

The extraction experiments were carried out at least in duplicate by equilibrating equal volumes (15mL each) of aqueous and pre-equilibrated organic phases for five minutes in separating funnels (60 mL capacity) at ambient temperature (~25 °C). This time was found sufficient for achieving equilibrium condition. The organic and aqueous phases were then allowed to settle and separated. The counter-current extraction was carried out in 125 mL separating fennel equilibrating 25 mL organic and 25 mL aqueous phase in counter-current mode. The 25 mL sample (aqueous as well as organic) from each stage was collected. The concentration of uranium and thorium in the aqueous phase was determined by ICPAES, EDXRF as well as titrometric techniques. The concentration of metal ions in organic phase was calculated by the difference in the metal ion concentration in the aqueous phase before and after extraction. The distribution ratio ($D_M$) of metal ions was calculated as:

$$D_M = \frac{[M]_{org}}{[M]_{aq}}$$  (1)

where, $[M]_{org}$ and $[M]_{aq}$ refer to metal ion concentration in organic and aqueous phases respectively, under equilibrium condition. Distribution ratio for stripping ($D_S$) for a ratio of organic: aqueous 1:1 was calculated using following equations:

$$D_S = \frac{[M]_{aq}}{[M]_{org}}$$  (2)

Separation factor ($\beta$) for two metal ions A and B having distribution ratio $D_A$ and $D_B$ was defined as:

$$\beta = \frac{D_A}{D_B}$$  (3)

Reproducibility of the experimental data and the material balance were within error limits of ±5 %.

**RESULTS AND DISCUSSIONS**

A new process for selective recovery of U(VI) from thorium cake was developed in our laboratory where the thorium cake was dissolved in nitric acid and separation of U(VI) was carried out using tris -2 ethyl hexyl phosphate (TEHP) diluted with n-paraffin. The recovery of Th(IV) from raffinate solution was
carried out using 1 M TiAP/n-paraffin as solvent. The present study mainly focus on the basic solvent extraction of U(VI), Th(IV) and REEs in HNO$_3$ medium employing TEHP, TiAP/n-paraffin. The results for U(VI)-Th(IV) separation were compared with TBP/n-paraffin under identical conditions. The study of U(VI) recovery from simulated monazite leach solution was carried out under wide experimental conditions such as variation of nitric acid concentration, variation of Th concentration, comparison with existing (established) solvent tri-n-butyl phosphate (TBP), construction of McCabe-Thiele diagram and counter-current extraction of U(VI) and Th(IV) under optimized conditions (Fig1 & 2). Based on these studies, selective recovery of U(VI) from monazite leach solution (HNO$_3$ medium) has been carried out using counter current extraction mode employing 0.1 M TEHP/n-paraffin as solvent (Table 2). The recovery of Th(IV) from raffinate solution was carried out using 5 stages counter current extraction mode employing 1 M TiAP/n-paraffin as solvent (Table 3). The stripping of U(VI) and Th(IV) was performed on 5 stages counter current stripping mode employing 0.05 M HNO$_3$. The U(VI) in stripped solution was precipitated using 30 % H$_2$O$_2$ at pH=3. Average particle size of the final precipitate was found to be ~33µm. Similarly the Th(IV) solution stripped from organic phase was precipitated as thorium-oxalate using sodium oxalate and converted to ThO$_2$ 800°C. The purity of final products was determined using ICPAES technique and the phase characterization was carried out employing XRD technique. Based on experimental results a solvent extraction process flow sheet has been proposed for the recovery of U(VI)-Th(IV) and REEs from monazite leach solution (Fig. 3).

CONCLUSIONS
Separation of U(VI)-Th(IV) from nitric acid medium was investigated using TEHP/n-paraffin and results were compared with same concentration of TBP/n-paraffin under identical conditions. The study shows the TEHP/n-paraffin is better solvent over TBP/n-paraffin for separation of U(VI)-Th(IV). Construction of McCabe-Thiele diagram for extraction of U(VI) from 2M HNO$_3$ medium containing 1g/L U(VI) using 0.2 M TEHP/n-paraffin shows that 4 numbers of stages were sufficient to recover all uranium from aqueous phase to organic phase. Similarly for stripping of U(VI) (1g/L) from 0.2M TEHP/n-paraffin loaded organic phase 2 stage were sufficient to strip all uranium to aqueous phase using water as strippant. Variation in TEHP/n-paraffin for selective recovery of U(VI) from nitric acid medium shows 0.1M TEHP/n-paraffin was optimum. Based on the optimized conditions, a 6 stage counter-current extraction and stripping study were performed to recover U(VI) from simulated monazite leach solution. The recovery of U(VI) from actual monazite leach solution was carried out in 5 stage counter current mode employing 0.1 M TEHP/n-paraffin. Similarly the Th(IV) from raffinate solution was recovered in 5 stage counter-current mode using 1 M TiAP/n-paraffin. Based on experimental results, a complete process flow sheet was proposed for selective recovery of U(VI), Th(IV) from monazite leach solution.
Fig. 1 McCabe-Thiele diagram for U extraction

Fig. 2 McCabe-Thiele diagram for Th extraction

Monazite Mineral

NaOH Treatment

Th, U, R.E Phosphate

Thorium Concentrate

Dissolved in HCl at pH ~3

RE Phosphate removal

U, Th, Hydroxide

Thorium Cake

Dissolved in HNO₃-HF (trace)

U, Th in 2M HNO₃ Solution

U: 1g/L, Th: 20g/L, RE: 17g/L

Solvent Extraction by 0.1 M TEHP/n-paraffin

U in 0.1M TEHP

Stripping by 0.05 M HNO₃

U in aqueous solution

H₂O₂

U ppt as UO₄.xH₂O

Th in aqueous phase

Solvent Extraction by 1M TiAP

Th in organic

Stripped with 0.05 M HNO₃

REEs in aqueous

Figure 3: Process flow-sheet for separation of U(VI)/Th(IV) during processing of Monazite mineral
Table 2: Counter-current extraction and separation of U(VI) from monazite leach solution (HNO₃ medium) using TEHP in n-paraffin; [HNO₃]: 2 M; [TEHP]: 0.1 M; [U(VI)]: 1.03 g/L; [Th(IV)]: 17 g/L; [REEs]: 17.2 g/L; Temperature: 298 K.

<table>
<thead>
<tr>
<th>No of stages</th>
<th>[U(VI)]₉₉₀₀ g/L</th>
<th>[U(VI)]ₐ₉₀₀ g/L</th>
<th>[Th(IV)]₉₉₀₀ g/L</th>
<th>[Th(IV)]ₐ₉₀₀ g/L</th>
</tr>
</thead>
<tbody>
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<td>0.042</td>
<td>0.31</td>
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<tr>
<td>2</td>
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<td>0.069</td>
<td>0.40</td>
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</tr>
<tr>
<td>3</td>
<td>1.263</td>
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<td>0.40</td>
<td>17.40</td>
</tr>
<tr>
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<tr>
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<td>1.662</td>
<td>0.235</td>
<td>0.50</td>
<td>20.30</td>
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</table>

Table 3: Counter-current extraction and separation of Th(IV) from monazite leach solution (1st cycle raffinate) using TiAP in n-paraffin; [HNO₃]: 2 M; [TiAP]: 1 M; [Th(IV)]: 20 g/L; [REEs]: 17.8 g/L; Temperature: 298 K.

<table>
<thead>
<tr>
<th>No of stages</th>
<th>[Th(IV)]₉₉₀₀ g/L</th>
<th>[Th(IV)]ₐ₉₀₀ g/L</th>
<th>[REEs]₉₉₀₀ g/L</th>
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<tbody>
<tr>
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<td>0.06</td>
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<tr>
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REFERENCES