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

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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 different 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 and PC88A as extractants from chloride medium. The major drawbacks of the existing amine
process are the crude and red oil formation, absence of suitable strippant and less uranium loading capacity of the
solvent [3-4].

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 using1 M TiAP/n-
paraffin as solvent. The present study mainly focus on the basic solvent extraction of U(VI), Th(IV) and REEs in
HNO3 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 (HNO₃ medium) has been carried out using counter current extraction mode employing 0.1 M TEHP/n-paraffin as solvent (Table 1). 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 2). The stripping of U(VI) and Th(IV) was performed on 5 stages counter current stripping mode employing 0.05 M HNO₃. The U(VI) in stripped solution was precipitated using 30 % H₂O₂ 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 ThO₂ 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.

Table 1: 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)]&lt;sub&gt;org&lt;/sub&gt; g/L</th>
<th>[U(VI)]&lt;sub&gt;aq&lt;/sub&gt; g/L</th>
<th>[Th(IV)]&lt;sub&gt;org&lt;/sub&gt; g/L</th>
<th>[Th(IV)]&lt;sub&gt;aq&lt;/sub&gt; g/L</th>
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<td>0.042</td>
<td>0.31</td>
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<tr>
<td>2</td>
<td>1.063</td>
<td>0.069</td>
<td>0.40</td>
<td>17.69</td>
</tr>
<tr>
<td>3</td>
<td>1.263</td>
<td>0.078</td>
<td>0.40</td>
<td>17.40</td>
</tr>
<tr>
<td>4</td>
<td>1.515</td>
<td>0.085</td>
<td>0.41</td>
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<tr>
<td>5</td>
<td>1.662</td>
<td>0.235</td>
<td>0.50</td>
<td>20.30</td>
</tr>
</tbody>
</table>

Table 2: Counter-current extraction and separation of Th(IV) from monazite leach solution (1<sup>st</sup> cycle raffinate) using TiAP in n-paraffin; [HNO₃]: 2 M; [TiAP]: 1 M; [Th(IV)]: 0.93 g/L; [REEs]: 17.8 g/L; Temperature: 298 K.

<table>
<thead>
<tr>
<th>No of stages</th>
<th>[Th(IV)]&lt;sub&gt;org&lt;/sub&gt; g/L</th>
<th>[Th(IV)]&lt;sub&gt;aq&lt;/sub&gt; g/L</th>
<th>[REEs]&lt;sub&gt;aq&lt;/sub&gt; g/L</th>
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<tbody>
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<tr>
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<tr>
<td>5</td>
<td>24.65</td>
<td>1.23</td>
<td>15.08</td>
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</table>

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 2 M HNO₃ 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.

REFERENCES
