Extraction of uranium from acidic media with a novel synergistic mixture of di-nonyl phenyl phosphoric acid and tri-\textit{n}-octyl phosphine oxide

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The extraction of uranium from aqueous acidic solutions of nitrate, perchlorate, sulphate, chloride and phosphate with a novel synergistic mixture of di-nonyl phenyl phosphoric acid (DNPPA) and tri-\textit{n}-octyl phosphine oxide (TOPO) in an aliphatic hydrocarbon diluent has been studied at varying concentrations of aqueous acids, extractant and uranium. The mole ratio [DNPPA]:[TOPO] has been found to have a significant effect on extraction of uranium. Maximum extraction was found at 2:1 mole ratio and no antagonistic effect was observed at higher concentration of TOPO. The extracted species has been found to be $\text{UO}_2(\text{HR}_2)_2\cdot\text{TOPO}$. The extraction order of uranium in aqueous media follows the sequence: perchlorate > nitrate > chloride > sulphate > phosphate. The selectivity of uranium with respect to other metals including Zn, Cu, Ni, Ca, and Fe has been investigated as a function of concentrations of sulphuric acid and extractant. Based on these findings, extraction of uranium has been carried out from leach liquor generated at an industrial plant, using 0.03 M DNPPA + 0.015 M TOPO with high recovery (>99%), selectivity and having added advantage of low inventory cost on extractants.

Keywords: Uranium, solvent extraction, DNPPA, TOPO, synergistic mixture

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The extraction of uranium with di-nonyl phenyl phosphoric acid (DNPPA) from wet process phosphoric acid (WPA) and merchant grade phosphoric acid (MGA) has been studied recently\cite{1-4}. The main interest has been focused on the effect of different parameters on the recovery of uranium from phosphoric acid medium\cite{5,6}. Studies with octyl phenyl phosphoric acid have been reported by Peppard and others\cite{7,8}. The extraction of uranium from dilute sulphate leach liquor is generally carried out by the ‘DAPEX’ process\cite{4} involving D2EHPA in combination with the synergistic reagent tri-\textit{n}-octyl phosphine oxide (TOPO) as an extracting reagent. D2EHPA has been studied for extraction of uranium from aqueous media\cite{10-15} in combination with various synergistic reagents. However, the extraction of uranium from nitrate, chloride, sulphate, perchlorate and phosphate with DNPPA has not been investigated. In the present investigation, the distribution of U(VI) between various acids and a solution of DNPPA + TOPO in an aliphatic diluent has been studied. The mechanism for extraction of U (VI) has been discussed on the basis of the results obtained. Single stage extraction tests were also carried out to see the feasibility of uranium recovery from sulphate leach liquor with dilute solution of DNPPA containing TOPO as synergistic reagent.

Experimental Procedure

Uranium solutions were prepared by dissolving pure uranium metal powder in required acids. The emf of the solution was measured to ensure that all uranium was in hexavalent state. Excess acid was eliminated by evaporation and then dilution with water to get 5g/L uranium solution. Known quantity of Zn, Cu, Co, and Ni metals were dissolved in nitric acid. Nitrate ions were then eliminated by fuming with sulphuric acid and solutions were made up to certain volume. A stock solution of KMnO\textsubscript{4} was prepared and suitable aliquot was reduced with hydrogen peroxide to obtain Mn solution. DNPPA, with \textgreater97% diester, was synthesized in this laboratory as described earlier\cite{2}. Analytical grade TOPO was used in this work. DNPPA+TOPO was diluted with an aliphatic diluent. The diluent was a high flash point aliphatic fraction from a kerosene refinery containing \textless1% aromatic hydrocarbons and having a flash point of 81°C. Extractions were carried out in glass separating funnels. Uranium was determined in the aqueous phase by measuring the optical density of uranium peroxide complex with spectrophotometer of...
Shimadzu model UV-2101 PC at 365 nm when concentration was in the range 0.1-1 g/L, while ICP method (Perkin-Elmer Plasma 400, 409.014 nm) was used for lower concentrations. The fluorimetric method was used for the determination of microgram concentrations of uranium in the presence of impurities such as Fe and Mn. Uranium concentration in organic phase was calculated by mass balance.

Results and Discussion

Extraction mechanism

The extraction behaviour of uranium by a solution of DNPPA in kerosene was investigated by the slope analysis technique. The general equation for the extraction of a divalent metal ion $M^{2+}$ by dialkyl phosphoric acid $H_2R_2$ can be presented as,

$$j M^{2+} + xj[H_2R_2]_{org} \leftrightarrow [MR_2(HR)_{2x-2}]_{org} + 2j H^+ \quad \ldots (1)$$

where org indicates organic phase and $j$ is the polymerization number of extracted species in the organic phase. By taking logarithm and rearranging the equation can be written as,

$$\log[M]_{org} = j (\log[M] - 2\log[H^+]) + xj \log[H_2R_2]_{org} + \log K_{ex} \quad \ldots (2)$$

where $[M]_{org}$ represents the total concentration of metal species in the organic phase and $K_{ex}$ is the equilibrium constant. The degree of polymerization of the metal and DNPPA complex ($j$) can be evaluated from the slope of the plot of $\log[M]_{org}$ against $(\log[M] - 2\log[H^+])$ at constant concentration of DNPPA in the organic phase. For generating such data, organic phase comprising 0.03 M DNPPA + 0.015 M TOPO was equilibrated separately with aqueous phase containing varying concentrations of uranium and different acids. As shown in Fig. 1, these plots yield straight lines of slope 1 for all the acids. This suggests that the extracted species is monomeric in the organic phase. The polymerization number of divalent metals with D2EHPA$^{16}$ and other extractants$^{17}$ have been determined by this procedure while for U-D2EHPA system isopiestic method was adopted. In these systems, monomer species were observed at low loading of metal in organic phase, similar to the present one.

As the complex of uranium(VI) with DNPPA is monomeric in nature, the general extraction equation reduces to the form,

$$M^{2+} + xH_2R_2 \leftrightarrow MR_2(HR)_{2x-2} + 2H^+ \quad \ldots (3)$$

Hence, it may be shown that

$$\log D = \log K_{ex} + x \log[H_2R_2] - 2\log[H^+] \quad \ldots (4)$$

where $D$ is the distribution ratio for the metal between the organic and the aqueous phases i.e., $[U]_{organic}/[U]_{aqueous}$. From a plot of $\log D$ versus $\log H^+$ (Fig. 2), straight lines of slope 2 were obtained for all the acids. Figure 2 shows that $D$ of uranium decreases with increasing acidity of the aqueous phase. These extractions were carried out up to 6 N acid strength.

![Fig. 1](image1.png)

**Fig. 1**—Evaluation of polymerization number of extracted species of uranium obtained from various acidic media. 1. Perchlorate 2. Chloride 3. Sulphate

![Fig. 2](image2.png)

**Fig. 2**—Effect of acid concentration on extraction of (a) uranium from various media. Perchlorate 2. Nitrate 3. Chloride 4. Sulphate 5. Phosphate (b) 6. Fe$^{3+}$ & 7. Fe$^{2+}$ in sulphate medium
but no enhanced extraction of uranium was observed above 3 N nitric acid, as was observed by Sato\textsuperscript{11} for D2EHPA system. To determine the number of free DNPPA molecules involved in the extracted species, the extraction of uranium at various concentrations of DNPPA was carried out at varying acidity. From the plot of $\log D + 2 \log[H^+]$ against $\log[(HR)_{2}]$, straight lines of slope 2 were obtained. Such plots, shown in Figs 2 and 3 confirm the above nature of extraction of U(VI) with DNPPA and indicate that $x=2$. Figure 3 also shows that the distribution ratio of uranium increases with the increase in DNPPA concentration. The curves shown in Figs 2 and 3 indicate that at comparable hydrogen ion concentration in the aqueous phase, $D$ increased in the order $\text{HClO}_4 > \text{HNO}_3 > \text{HCl} > \text{H}_2\text{SO}_4$. The variation in $D$ can be qualitatively explained in terms of the relative complexing\textsuperscript{18,19} ability of the anions concerned.

It is known that when a neutral organo phosphorus compound is added to the organic phase containing D2EHPA, there is an enhancement in the extraction of uranium. This effect follows the sequence: phosphate $<$ phosphonate $<$ phosphinate $<$ phosphine oxide\textsuperscript{20}. The basicity of TOPO makes it very favourable for this purpose. In case of DNPPA-TOPO-phosphate system, the mole ratio was found to be 2:1 (DNPPA:TOPO), which yielded maximum value of $D$ for uranium\textsuperscript{2} which is different from other systems\textsuperscript{14}. Hence, a study was carried out as part of present investigations to explore the behaviour of uranium in different acid media when the synergic extractant mixture DNPPA and TOPO in an aliphatic diluent was used.

The variation of the $D$ value with changing concentration of TOPO at DNPPA concentration of 0.03 M from 2 g/L uranium solution in various media is given in Fig. 4. The value of $D$ initially rises steeply with increasing TOPO concentration, then the curve flattens in all the cases. The increase in $D$ value is attributed to adduct formation. To determine the number of TOPO molecules involved in the extracted species, plots of $\log[D]$ versus $\log[\text{TOPO}]$ were constructed for different acids at constant concentration of DNPPA (0.03 M) as shown in Fig. 5. It was observed that the slopes of lines were $1.1 \pm 0.1$, up to 0.02 M TOPO concentration. This indicates that
one mole of TOPO is involved for the extraction of one mole of uranium. Based on the results the extraction equilibrium can be presented as,

$$\text{UO}_2^{2+} + 2(\text{HR})_2^+ + \text{TOPO} \leftrightarrow \text{UO}_2(\text{HR}_2)_2\text{.TOPO} + 2\text{H}^+ \ldots(5)$$

**Selectivity of uranium with respect to other metals**

The industrial leach solution contains many metal impurities such as iron, base metals, calcium, etc. Tests were performed to study the effect of acid and DNPPA concentration on selectivity and yield of uranium from an industrial leach solution.

**Effect of acid concentration**

Sulphate solution containing Zn, Cu, Co, and Ni (0.2 M) and nitrate solution of Ca (0.2 M) were equilibrated in 1:1 phase ratio with 0.2 M DNPPA at varying pH. The results plotted in Fig. 6 indicate that the extraction of these metals increases in the order as Ni < Co < Cu < Ca < Zn and extraction increases as the pH of equilibrium aqueous phase increases. However, at low pH (~1) the $D$ values of these metals are very low and the impurities are not expected to compete with the extraction of uranium. The extraction of Fe$^{2+}$ and Fe$^{3+}$ (from 2 g/L solution) were carried out in sulphate medium with 0.03 M DNPPA + 0.015 M TOPO in 1:1 phase ratio at different sulphuric acid concentrations. Results shown in Fig. 2 indicate that $D$ value decreases with increase in acid concentration of aqueous phase. It appears that at lower acidity (1-2 N) the separation factor between U and Fe is high enough (~10) to separate them in counter-current extraction system.

**Effect of DNPPA on separation of iron**

The sulphate solution containing 2 g/L iron (III), 0.5 g/L uranium (VI) and 0.5 N H$_2$SO$_4$ was equilibrated in 1:1 phase ratio with DNPPA of varying concentrations at [DNPPA]:[TOPO] mole ratio of 2:1. The results given in Table 1 show that $D$ of uranium increases steeply, while $D$ of iron increases from 0.26 to 0.63. $D$ of iron is slightly suppressed in presence of uranium. To minimize the loss of DNPPA solvent in the aqueous phase in large scale operations, a lower concentration (0.03 M) is preferred.

**Uranium extraction from leach liquor**

Leach liquor generated from uranium ore contains many metals and its typical composition is shown in Table 2. This solution was equilibrated with DNPPA of different concentrations, in 1:1 phase ratio at varying concentrations, of sulphuric acid. Results given in Table 3 indicate that uranium extraction is almost complete (>96%) in all the cases. Manganese extraction is found to be negligible. Iron extraction

<table>
<thead>
<tr>
<th>Concentration of DNPPA (M)</th>
<th>$D$ from feed 1</th>
<th>$D$ from feed 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>Fe$^{2+}$</td>
<td>Fe$^{3+}$</td>
</tr>
<tr>
<td>0.01</td>
<td>0.2</td>
<td>0.28</td>
</tr>
<tr>
<td>0.03</td>
<td>4.7</td>
<td>0.49</td>
</tr>
<tr>
<td>0.04</td>
<td>55.0</td>
<td>0.54</td>
</tr>
<tr>
<td>0.05</td>
<td>509.0</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Aqueous feed—Feed 1: 2 g/L Fe$^{3+}$ + 0.5 g/L U + 0.5 N H$_2$SO$_4$
Feed 2: 2 g/L Fe$^{3+}$ + 0.5 N H$_2$SO$_4$

Organic phase—DNPPA concentration varied, mole ratio = 2:1 (DNPPA:TOPO)

Table 2: A typical composition of leach liquor produced from a uranium ore

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration (g/L)</th>
<th>Constituent</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U$_3$O$_8$</td>
<td>0.3-0.4</td>
<td>Sulphate</td>
<td>16-18</td>
</tr>
<tr>
<td>Fe (Total)</td>
<td>1-1.25</td>
<td>Chloride</td>
<td>0.3-0.4</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.3</td>
<td>Silica</td>
<td>0.8-1.0</td>
</tr>
<tr>
<td>Mn</td>
<td>0.4-0.6</td>
<td>Cu</td>
<td>0.03</td>
</tr>
<tr>
<td>Ni</td>
<td>0.1-0.2</td>
<td>Ca</td>
<td>0.5-0.6</td>
</tr>
</tbody>
</table>

Leach liquor: pH ~2, emf: 460 mV
was observed to decrease as the acidity of the feed solution was increased. Iron can be removed by scrubbing with 1 M H₂SO₄.

**Conclusion**

The extraction mechanism of uranium with DNPPA in combination with TOPO has been established from different acidic media. The extraction order of uranium from these media has been found as perchlorate > nitrate > chloride > sulphate > phosphate. Based on these results extraction of uranium from samples of leach liquor generated from an ore has been carried out and >96% recovery of uranium is obtained.

**Acknowledgement**

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**References**


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**Table 3**—Effect of DNPPA and acid concentrations on extraction of uranium, manganese and iron

<table>
<thead>
<tr>
<th>DNPPA concn. (M)</th>
<th>pH 2</th>
<th>1 N acid</th>
<th>2 N acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>Fe</td>
<td>Mn</td>
<td>U</td>
</tr>
<tr>
<td>0.03</td>
<td>&gt;99</td>
<td>90</td>
<td>5</td>
</tr>
<tr>
<td>0.05</td>
<td>&gt;99</td>
<td>95</td>
<td>7</td>
</tr>
<tr>
<td>0.10</td>
<td>&gt;99</td>
<td>98</td>
<td>9</td>
</tr>
</tbody>
</table>

Aqueous Feed: Uanyl sulphate leach liquor from industrial plant

Organic feed: DNPPA + TOPO (mole ratio = 2:1)