Impact of gamma-irradiation on the palladium behaviour in the PUREX process
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**Impact of γ-irradiation on the palladium behaviour in the PUREX process**

**Context:**
The PUREX process uses 30%$_{\text{MO}}$ tri-n-butylphosphate (TBP) diluted in TetraPropylen Hydrogen (TPH, an hydrocarbon diluent) to selectively extract uranium(VI) and plutonium(VI) towards fission products. During the different extraction cycles, solvent degradation products of the solvent are formed due to radiolysis. Very few studies report the impact of the radiolysis on the palladium behaviour. The aim of this work is to investigate the effect of the radiolysis on the Pd behaviour.

**Bibliographic results on the impact of γ-irradiation of the TBP-alkane solvent:**

Identification of degradation products (DP) [1]

<table>
<thead>
<tr>
<th>DP</th>
<th>Structure</th>
<th>Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDBP</td>
<td>(HOCC-HOC)(HOCH$_2$PO)</td>
<td>Diluent DP</td>
</tr>
<tr>
<td>TBP DP</td>
<td>(C-HC)OP(C-HC)OP(C-HC)</td>
<td>mixture of TBP and diluent DP</td>
</tr>
</tbody>
</table>

Degradation products formed in the organic phase for a TBP-alkane / nitric acid aqueous solution system

**Experiments: γ-irradiation of the solvent in presence of palladium:**

TBP 30% - TPH / HNO$_3$ 1 and 3 mol/L Pd(NO$_3$)$_2$ ~ 2 – 10 g/L Irradiated mixture at 500 kGy

**Characterizations of the precipitates:**

**Characterization of the solid**

**XRD analysis: powder pattern**

![XRD pattern](image)

Powder pattern of the precipitated species is close to that of commercial compound Pd(CN)$_2$.

**Characterization of the solid after solubilisation**

**RMN analysis**

precipitate 4 partially dissolved in deuterated DMSO - $^{13}$C – H

-172 ppm -150 ppm

C=O C=N

![RMN spectrum](image)

Presence of C=O at -172 ppm

Presence of C=N at -150 ppm

**Conclusions and Outlook:**

- Presence of functions in the solids: cyanide (similarity with Pd(CN)$_2$), carboxylate and ammonium
- Isolation of different compounds present in the precipitate: selective dissolution
- Mechanism of formation of these precipitates

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