The next figure presents a simplified flow sheet of a first cycle of a dissolution solution of an irradiated PWR fuel, where the following operations are realized by liquid-liquid extraction with TBP:

- Co-extraction U + Pu, separation of FP (extractors A and B)
- Partition U/Pu (extractors C and D) by reducing extraction of Pu under the action of U(IV)
- Reextraction U (Extractor E)
FEED
U(VI) = 250 g/L
Pu(IV) = 2.55 g/L
FP = 6.78 g/L
HNO₃ = 3M
3,820 L/t

AQ WASH
HNO₃ = 3M
2,300 L/t

ORG WASH
TBP 30% Vol
Hyfrane
1,600 L/t

USED
SOLVENT
TBP Hyfrane
U = 0.05 g/L
Pu = 1.10⁻⁴ g/L
HNO₃ = 4 10⁻³M
12,500 L/t

EXTRACTION
U + Pu
A

WASH
FP
B

WASH
U
C

REEXTRACTION
Pu
D

REEXTRACTION
U
E

Solvent
TBP
30% Vol
Hyfrane
10,900 L/t

Raffinate
U = 0.05g/L
Pu = 0.002 g/L
FP = 4.23 g/L
HNO₃ = 2.634M
6,120 L/t

Sol. Purified Pu
U = 0.1g/L
Pu = 6.133 g/L
HNO₃ = 1.3 M
1,586 L/t

Sol. Purified Pu
U(IV) = 30.5g/L
HNO₃ = 0.362 M
1,586 L/t

Sol. Purified U
U = 65.94g/L
Pu = 60.10⁻⁹ g/L
HNO₃ = 0.066 M
15,200 L/t
Questions

1) Write the equations of the principal reactions that involve U and Pu in the different extraction columns (A, C, D, E).

2) Justify the concentrations of HNO₃ in the different aqueous flows that enter the extraction columns (flows 1 and 4, flow 6 and flow 8).

3) Calculate the ratio organic flow / aqueous flow in each extraction column.

4) Establish the global mass balance for U, Pu and HNO₃ (Σ entering flux = Σ exiting flux).

5) Calculate the yield of purified U and Pu.

6) Calculate the decontamination factor FD of Pu and U of the purified Pu solution.
Equations

Column A

\[ UO_2^{2+} + 2NO_3^- + 2 \text{TBP} \rightleftharpoons UO_2(NO_3)_2(TBP) \]

\[ Pu^{4+} + 4NO_3^- + 2 \text{TBP} \rightleftharpoons Pu(NO_3)_4(TBP) \]

Column C

\[ U^{4+} + 4NO_3^- + 2 \text{TBP} \rightleftharpoons U(NO_3)_4(TBP) \]

\[ UO_2^{2+} + 2NO_3^- + 2 \text{TBP} \rightleftharpoons UO_2(NO_3)_2(TBP) \]

Column D

\[ Pu(NO_3)_4(TBP) \rightleftharpoons Pu^{4+} + 4NO_3^- + 2 \text{TBP} \]

\[ 2Pu^{4+} + U^{4+} + 2H_2O \rightleftharpoons 2Pu^{3+} + UO_2^{2+} + 4H^+ \]

Column E

\[ UO_2(NO_3)_2(TBP) \rightleftharpoons UO_2^{2+} + 2NO_3^- + 2 \text{TBP} \]
Justification HNO$_3$ concentration

- **Flow 1 and 4 [HNO$_3$] = 3M**, We have an adequate concentration of NO$_3^-$ to get a D U(VI) and D Pu(IV) sufficiently high.

- **Flow 6, [HNO$_3$] = 0.362M**, Favors the decrease of D Pu(IV) and increase the reduction reaction of Pu(IV) to Pu(III) by U(IV), a lower acidity may induce the potential hydrolysis and polymerization of Pu(IV).

- **Flow 8 [HNO$_3$] = 0.02M**, A low acidity concentration decreases the D U(VI), so initiates the reextraction of U(VI).
# Ratio O/Aq

<table>
<thead>
<tr>
<th>Column</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Flow (L/t)</td>
<td>10900</td>
<td>10900</td>
<td>1600</td>
<td>12500</td>
<td>12500</td>
</tr>
<tr>
<td>Aqueous Flow (L/t)</td>
<td>6120</td>
<td>2300</td>
<td>1586</td>
<td>1586</td>
<td>15200</td>
</tr>
<tr>
<td>Ratio Organic/Aqueous</td>
<td>1.781</td>
<td>4.739</td>
<td>1.0088</td>
<td>7.88</td>
<td>0.822</td>
</tr>
</tbody>
</table>
RATIO Organic Flow/Aqueous Flow

**FEED**
- U(VI) = 250 g/L
- Pu(IV) = 2.55 g/L
- FP = 6.78 g/L
- HNO₃ = 3M
- Used Solvent: TBP Hyfrane
- U = 0.05 g/L
- Pu = 1.10⁻⁴ g/L
- HNO₃ = 4 x 10⁻³ M

**AQ WASH**
- HNO₃ = 3M
- Flow: 2,300 L/t

**ORG WASH**
- TBP 30% Vol
- Flow: 1,600 L/t

**USED SOLVENT**
- TBP Hyfrane
- Flow: 12,500 L/t

**EXTRACTION U + Pu**
- U = 0.05 g/L
- Pu = 6.133 g/L
- HNO₃ = 1.3 M
- Flow: 10,900 L/t

**WASH FP**
- FP = 6.78 g/L
- Flow: 6,120 L/t

**WASH U**
- U = 0.1 g/L
- Pu = 60.10⁻⁹ g/L
- HNO₃ = 0.066 M
- Flow: 15,200 L/t

**REEXTRACTION Pu**
- U = 0.05 g/L
- Pu = 0.002 g/L
- FP = 4.23 g/L
- HNO₃ = 2.634 M
- Flow: 1,586 L/t

**REEXTRACTION U**
- U(IV) = 30.5 g/L
- Pu = 60.10⁻⁹ g/L
- HNO₃ = 0.362 M
- Flow: 15,200 L/t
FEED

U(Ⅵ) = 250 g/L
Pu(IV) = 2.55 g/L
FP = 6.78 g/L
HNO₃ = 3M

3,820 L/t

AQ WASH

HNO₃ = 3M

2,300 L/t

ORG WASH

TBP 30% Vol

Hyfrane

1,600 L/t

USED SOLVENT

TBP Hyfrane

U = 0.05 g/L
Pu = 1.10^-4 g/L
HNO₃ = 4 10^-3 M

12,500 L/t

EXTRACTION

U + Pu

HEX

Raffinate

U = 0.05 g/L
Pu = 0.002 g/L
FP = 4.23 g/L
HNO₃ = 2.634 M

6,120 L/t

WASH FP

WASH U

REEXTRACTION Pu

Sol. REEX Pu

U(IV) = 30.5 g/L
HNO₃ = 0.362 M

1,586 L/t

Sol. Purified Pu

U = 0.1 g/L
Pu = 6.133 g/L
HNO₃ = 1.3 M

1,586 L/t

REEXTRACTION U

Sol. REEX U

U = 65.94 g/L
Pu = 60.10^-9 g/L
HNO₃ = 0.066 M

15,200 L/t

Mass Pu enter 9.741 kg/t

Mass Pur. Pu 9.7269 kg/t

Yield Pu

9.7269 * 100
9.741
= 99.85%
Decontamination factor Pu(U)

Flow 7
\([\text{Pu}]_{\text{final}}/[\text{U}]_{\text{final}} = 6.133/0.1 = 61.33\) (Flow 7)

Flow 1
\([\text{Pu}]_{\text{ini}}/[\text{U}]_{\text{ini}} = 2.55/250 = 0.0102\) (Flow 1)

DF Pu(U) = 61.33 / 0.0102 = 6012.7