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TUNGSTEN RECOVERY AND ARSENIC REMOVAL FROM SECONDARY RESOURCES

DEEP EUTETIC SOLVENTS IN THE ELECTRODIALYTIC PROCESS
SCOPE

Panasqueira Mine, Covilhã, PT
SCOPE

Panasqueira Mine, Covilhã, PT

Arsenic

Mining residues
SCOPE

Panasqueira Mine, Covilhã, PT

Arsenic

Tungsten

Mining residues
SCOPE

How to remove harmful compounds & recover critical raw materials from secondary resources?

Panasqueira Mine, Covilhã, PT

Arsenic

Tungsten

Mining residues
How to remove harmful compounds & recover critical raw materials from secondary resources?

SCOPE

Panasqueira Mine, Covilhã, PT

Arsenic

Tungsten

Mining residues

Electro-based technologies

Deep Eutetic Solvents
Mining residues

How to remove harmful compounds & recover critical raw materials from secondary resources?

Electro-based technologies

Deep Eutetic Solvents

Both techniques combined!

SCOPE

Arsenic

Tungsten

Panasqueira Mine, Covilhã, PT

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How to remove harmful compounds & recover critical raw materials from secondary resources?

Treated mining residues for reuse in the construction sector

SCOPE

Panasqueira Mine, Covilhã, PT

Arsenic

Tungsten

Mining residues

Electro-based technologies

Deep Eutetic Solvents

Treated mining residues for reuse in the construction sector
Sample

Rejected fraction from sludge circuit (tube output; pumped directly to the Panasqueira dam)

➔ Low conductivity

0.8 ± 0.4 mS/cm

➔ Acidic pH

5.3 ± 0.5

➔ Arsenic content

As: 1675 ± 564 mg/kg

➔ Tungsten content

W: 130 ± 31 mg/kg

➔ Other elements of interest

Cu: 731 ± 270 mg/kg

Sn: 38 ± 9 mg/kg
X-Ray Fluorescence (XRF)
Semi-Quantitative Data (%)

- Si: 67.6%
- Al: 18.6%
- P, Cr, Mn, Se, Rb, Sr, Y, Zr, Nb, Cd, Sn, Ba, Pb: 0.4%
- W: 0.3%
- As: 0.6%

Other elements include S, K, Ca, Ti, Fe, Cu, Zn, As, W.
DEEP EUTETIC SOLVENTS

Deep Eutetic Solvents = (DES)

<table>
<thead>
<tr>
<th></th>
<th>Ionic Liquids</th>
<th>Deep Eutetic Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low price</td>
<td>X</td>
<td>✓</td>
</tr>
<tr>
<td>Low toxicity</td>
<td>X</td>
<td>✓</td>
</tr>
<tr>
<td>100% atom economy</td>
<td>X</td>
<td>✓</td>
</tr>
<tr>
<td>Biodegradable</td>
<td>X</td>
<td>✓</td>
</tr>
<tr>
<td>Low vapor pressure</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Low volatility</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Acids, amides, amines and alcohols as liquid \( \leq 100 \, ^\circ C \)

Quaternary ammonium or metal salt + Hydrogen bond donor (HDB)
# Deep Eutectic Solvents (DES)

Deep Eutectic Solvents are mixtures of quaternary ammonium or metal salts and hydrogen bond donors (HDBs) that form a liquid at temperatures lower than the individual melting points of the components.

**Why DES?**

<table>
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<th>Ionic Liquids</th>
<th>Deep Eutectic Solvents</th>
</tr>
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<tbody>
<tr>
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<td>Low vapor pressure</td>
<td>✓</td>
</tr>
<tr>
<td>Low volatility</td>
<td>✓</td>
</tr>
</tbody>
</table>

- **Acids, amides, amines and alcohols as liquid ≤ 100 °C**
- **Why DES?**
  - Low price
  - Low toxicity
  - 100% atom economy
  - Biodegradable
  - Low vapor pressure
  - Low volatility

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Electrokinetic (EK) and Electrodialytic (ED) treatments consist in a low current density (mA/cm²) application between a pair of electrodes to promote removal/separation of substances, with an ionic exchange membrane interposed in the ED treatment.

(A) 3 compartments ED cell
(B) & (C) 2 compartments ED cell

AEM - Anionic exchange membrane
CEM - Cationic Exchange membrane
GOALS

Mining residues (MR)

Arsenic

Tungsten
GOALS

Mining residues (MR) → Arsenic → Tungsten
GOALS

1. Selection of the most efficient DES for As and W extraction from the matrix
GOALS

1. Selection of the most efficient DES for As and W extraction from the matrix

2. Potential of the EK process combined with DES to improve As and W extraction from the matrix
**GOALS**

1. Selection of the most efficient DES for As and W extraction from the matrix

2. Potential of the EK process combined with DES to improve As and W extraction from the matrix

3. Feasibility of the ED process to separate As and W in a compartment apart from the matrix
Selection of the most efficient DES for As and W extraction from the matrix

**DES tested**

- **ChCl:MA** - Choline Chloride:Malonic Acid (1:2)
- **ChCl:OA** - Choline Chloride:Oxalic Acid (1:1)
- **ChCl:LA** - Choline Chloride:Lactic Acid (1:2)
- **PA:U** - Propionic Acid:Urea (2:1)

**DES + MR**

- Liquid/solid = 9
- Stirring
- 10 days
Potential of the EK process combined with DES to improve As and W extraction from the matrix

DES tested with higher As and W extraction

\[ \text{DES} + \text{MR} + \text{H}_2\text{O} \]

(1.5% ChCl:MA & 1.5% ChCl:OA)

50 & 100 mA
Liquid/Solid=9
Stirring
4 days

\[ \text{➔ ChCl:MA} - \text{Choline Chloride:Malonic Acid (1:2)} \]
\[ \text{➔ ChCl:OA} - \text{Choline Chloride:Oxalic Acid (1:1)} \]

\[ \uparrow \text{As} \]

\[ \uparrow \text{W} \]
Feasibility of the ED process to separate As and W in a compartment apart from the matrix

DES tested with higher As and W extraction

- ChCl:MA - Choline Chloride:Malonic Acid (1:2)
- ChCl:OA - Choline Chloride:Oxalic Acid (1:1)

50 & 100 mA
Liquid/Solid=9
Electrolyte 0.01 M NaNO₃
Stirring
4 days

DES + MR +H₂O
(1.5% ChCl:MA & 1.5% ChCl:OA)
Selection of the most efficient DES for As and W extraction from the matrix

- ChCl:MA
- ChCl:OA
- ChCl:LA
- ChCl:PA

Arsenic and Tungsten extraction

- ChCl:MA
  - As: 12%
  - W: 5%
- ChCl:OA
  - As: 7%
  - W: 9%
- ChCl:LA
  - As: 2%
  - W: 1%
- ChCl:PA
  - As: 7%
  - W: 5%
RESULTS & DISCUSSION

Selection of the most efficient DES for As and W extraction from the matrix

Arsenic and Tungsten extraction

<table>
<thead>
<tr>
<th>DES</th>
<th>As (%)</th>
<th>W (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ChCl:MA</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>ChCl:OA</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>ChCl:LA</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>ChCl:PA</td>
<td>7</td>
<td>5</td>
</tr>
</tbody>
</table>
RESULTS & DISCUSSION

Potential of the EK process combined with DES to improve As and W extraction from the matrix

Extraction percentages in relation to DES experiments without current

-2%  50 mA - ChCl:OA  
+ 3%  

+ 21%  100 mA - ChCl:OA

+ 7%  

+ 6%  50 mA - ChCl:MA

+ 0.4%  

+ 10%  100 mA - ChCl:MA

-2%  

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RESULTS & DISCUSSION

Potential of the EK process combined with DES to improve As and W extraction from the matrix.

Extraction percentages in relation to DES experiments without current:

- 50 mA - ChCl:OA: -2% (As) +3% (W)
- 100 mA - ChCl:OA: +21% (As) +7% (W)
- 50 mA - ChCl:MA: +6% (As) +0.4% (W)
- 100 mA - ChCl:MA: +10% (As)
VOLTAGE, pH & CONDUCTIVITY CONTROL

**Voltage**

- 50 mA - ChCl:OA
- 50 mA - ChCl:MA
- 100 mA - ChCl:OA
- 100 mA - ChCl:MA

**pH**

**Conductivity**

- Voltage (V)
- Time (hours)

- pH
- Time (hours)

- Conductivity (mS/cm)
- Time (hours)
Feasibility of the ED process to separate As and W in a compartment apart from the matrix

Compartments distribution of As and W extracted contents

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>W</th>
<th>As</th>
<th>W</th>
<th>As</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>4%</td>
<td>2%</td>
<td>18%</td>
<td>5%</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>(Liquid phase)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Electrolyte content</td>
<td></td>
</tr>
<tr>
<td>50 mA - ChCl:OA</td>
<td>6%</td>
<td>5%</td>
<td>6%</td>
<td>1%</td>
<td>4%</td>
<td>3%</td>
</tr>
<tr>
<td>100 mA - ChCl:OA</td>
<td>4%</td>
<td>5%</td>
<td>17%</td>
<td>7%</td>
<td>21%</td>
<td>4%</td>
</tr>
<tr>
<td>50 mA - ChCl:MA</td>
<td>15%</td>
<td>6%</td>
<td>5%</td>
<td>6%</td>
<td>4%</td>
<td>4%</td>
</tr>
<tr>
<td>100 mA - ChCl:MA</td>
<td>15%</td>
<td>6%</td>
<td>21%</td>
<td>4%</td>
<td>1%</td>
<td>3%</td>
</tr>
</tbody>
</table>

RESULTS & DISCUSSION

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Removed - Liquid phase + electrolyte contents; Separated - electrolyte content
RESULTS & DISCUSSION

Feasibility of the ED process to separate As and W in a compartment apart from the matrix

Compartments distribution of As and W extracted contents

Higher W separation

Higher As separation

<table>
<thead>
<tr>
<th>As</th>
<th>W</th>
<th>As</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mA - ChCl:OA</td>
<td>Sample compartment (Liquid phase)</td>
<td>6%</td>
<td>2%</td>
</tr>
<tr>
<td>100 mA - ChCl:OA</td>
<td>Electrolyte compartment</td>
<td>17%</td>
<td>15%</td>
</tr>
<tr>
<td>50 mA - ChCl:MA</td>
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</tbody>
</table>

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Removed - Liquid phase + electrolyte contents; Separated - electrolyte content
RESULTS & DISCUSSION

Feasibility of the ED process to separate As and W in a compartment apart from the matrix

Compartment distribution of As and W extracted contents

Total of 35% of As extracted

Total of 22% of W extracted

<table>
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</tr>
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<td>18%</td>
<td>17%</td>
</tr>
<tr>
<td>15%</td>
<td>7%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>50 mA - ChCl:OA</th>
<th>100 mA - ChCl:OA</th>
</tr>
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<tbody>
<tr>
<td>Sample compartment (Liquid phase)</td>
<td>Electrolyte compartment</td>
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</table>

<table>
<thead>
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<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
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</tr>
<tr>
<td>17%</td>
<td>21%</td>
</tr>
<tr>
<td>4%</td>
<td>3%</td>
</tr>
</tbody>
</table>

Removed - Liquid phase + electrolyte contents; Separated - electrolyte content
ELECTROLYTE BEHAVIOR

Mass and Percentage of elements reaching the electrolyte along the experiments

Arsenic content

Tungsten content

Arsenic accumulated percentage in the electrolyte

Tungsten accumulated percentage in the electrolyte

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Percentage of elements from the total As and W extracted that reached the electrolyte.
Percentage of elements from the total As and W extracted that reached the electrolyte

<table>
<thead>
<tr>
<th>Current (mA)</th>
<th>ChCl:OA</th>
<th>ChCl:MA</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>61%</td>
<td>48%</td>
</tr>
<tr>
<td>100</td>
<td>75%</td>
<td>32%</td>
</tr>
<tr>
<td>50</td>
<td>45%</td>
<td>38%</td>
</tr>
<tr>
<td>100</td>
<td>82%</td>
<td>58%</td>
</tr>
</tbody>
</table>
CONCLUSIONS

1. Selection of the most efficient DES for As and W extraction from the matrix

- Different DES demonstrated higher extraction efficiencies for different elements
  - ChCl:MA (1:2) extracted a maximum of 12% for As
  - ChCl:OA (1:1) extracted a maximum of 9% for W
CONCLUSIONS

Potential of the EK process combined with DES to improve As and W extraction from the matrix

→ Deep Eutetic solvents and EK treatment synergy potentiated the extraction

- As extraction increased 21% (100 mA, ChCl:OA)
- W extraction increased 10% (100 mA, ChCl:MA)

Compared to DES experiments with no current
CONCLUSIONS

3. Feasibility of the ED process to separate As and W in a compartment apart from the matrix

→ ED treatment enable to separate As and W, improving the migration of the elements from the matrix to the electrolyte compartment

- From the total As extracted, 82% (100 mA, ChCl:MA) migrated to the electrolyte

- From the total W extracted, 75% (50 mA, ChCl:OA) migrated to the electrolyte
Thank you!

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