The extraction of elements from secondary mining resources in electrodialytic systems

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Problem

Population growth implied the need of more raw materials to serve inhabitants

- Low ore grades promoted high disposal rates of residues at mining sites
- The processes involved release intense CO₂ emissions
- Overexploitation of primary ore resources generated raw materials scarcity
Tungsten (W)

Critical raw material included in EU list (2020) as one of the 30 Critical Raw Materials

Transition metal used in

- Cement carbide
- Alloys
- Steels

Primary sources of W are scheelite (CaWO₄) and wolframite (Fe,Mn)WO₄
Secondary mining resources

The Panasqueira Mine, Covilhã, Portugal

- Secondary source of critical raw materials - W
- Presence of contents of Arsenic (As), a harmful metalloid

The challenge

To develop sustainable strategies to recover W and remove As from secondary resources
**Electrodialytic process (ED)**

The ED technology is applied to remove inorganic and/or organic substances from liquid and solid matrices.

Based on the application of a low-level current intensity, between pairs of electrodes, the removal of substances from a matrix is promoted.

- Ion exchange membranes are used to separate the contaminated matrix.
- The water electrolysis at inert electrodes generates an acidic media at the anode (H⁺) and an alkaline media at the cathode (OH⁻).
Deep eutectic solvents (DES)

Natural solvents applied for the extraction of metals from environmental matrices

DES = Quaternary ammonium or metal salt + hydrogen bond donor

1 Acids, amides, amines, and alcohols as liquid < 100 ° C

<table>
<thead>
<tr>
<th></th>
<th>Ionic liquids</th>
<th>Deep eutectic solvents (natural products)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low price</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>Low toxicity</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>100% atom economy</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>Biodegradable</td>
<td>✗</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>
Goals

Electrodialytic technologies and DES were tested to:

1. **Extract elements from Panasqueira mine secondary resources**

2. **Understand the species behavior in the reactor and improve the efficiency of the ED system**
Sample characterisation

Rejected fraction from the sludge circuit, that is directly pumped to the Panasqueira dam

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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Conductivity</td>
<td>0.8 ± 0.4 mS/cm</td>
</tr>
<tr>
<td>pH</td>
<td>5.3 ± 0.5</td>
</tr>
<tr>
<td>Arsenic</td>
<td>1675 ± 564 mg/kg</td>
</tr>
<tr>
<td>Tungsten</td>
<td>130 ± 31 mg/kg</td>
</tr>
<tr>
<td>Copper</td>
<td>731 ± 270 mg/kg</td>
</tr>
<tr>
<td>Tin</td>
<td>38 ± 9 mg/kg</td>
</tr>
</tbody>
</table>
Desorption tests of the mining residues

- Generally, elements desorption from mining residues were higher at pH values below 2.
Application of the electrodialytic technology to mining residues

Electrodialytic process tested for As, Cu, Sn and W extraction from mining residues

Highest extraction of elements achieved in a system including

✓ 3 compartment reactor
✓ 5 days of experiment
✓ Current intensity of 100 mA
✓ NaCl as supporting electrolyte due to the low conductivity of the sample (0.3 mS/cm)

Extraction ratios
As $\rightarrow$ 63%
Cu $\rightarrow$ 13%
Sn $\rightarrow$ 10%
W $\rightarrow$ 13%
Application of the electrodialytic technology to mining residues

Electrodialytic process tested for As, Cu, Sn and W extraction from mining residues

<table>
<thead>
<tr>
<th>Component</th>
<th>pH</th>
<th>Conductivity (mS/cm)</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>6.8 ± 0.2</td>
<td>12.5 ± 0.5</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>Central (sample)</td>
<td>5.3 ± 0.7</td>
<td>4.5 ± 1.0</td>
<td>12.6 ± 1.6</td>
</tr>
<tr>
<td>Anode</td>
<td>6.8 ± 0.2</td>
<td>1.5 ± 0.1</td>
<td>0.7 ± 0.1</td>
</tr>
</tbody>
</table>
As, Cu, Sn and W distribution in the ED reactor after the ED experiments

- As was detected in the anolyte (28%)
- Cu (12%) and W (11%) were mainly detected at the anode end
- Sn was detected in both electrolyte compartments in the same proportion (2%)
Application of the electrodialytic technology and DES to mining residues

Extraction of W and As from mining residues

Tested combinations for Arsenic and Tungsten extraction

✔ Choline chloride/ malonic acid (1:2)
✔ Choline chloride/ oxalic acid (1:1)
✔ Choline chloride/ lactic acid (1:2)
✔ Propionic acid/ urea (2:1)

Coupling ED and DES promote the extraction of 35% of As and 22% of W
Application of the electrodialytic technology and DES to mining residues

Mass and percentage of As and W reaching the electrolyte along the experiments
Application of the electrodialytic technology and DES to mining residues

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

✓ The reuse of mining residues can decrease consumption of primary resources and promote improvements in the sustainability of mining industries

✓ The application of the electrodialytic process and DES suggests new possibilities for the recovery of critical raw materials and the removal of harmful compounds from secondary mine resources
  ✓ Different DES demonstrated higher extraction efficiencies for different elements
  ✓ DES plus ED process synergy may potentiate the extraction of elements
  ✓ ED treatment promote the separation of As and W, improving the migration of the elements from the matrix to the electrolyte compartment
Thank you!

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