Electrolytic treatment of highly contaminated effluents from copper smelters

S. Stopić; A. Widigdo; B. Friedrich

IME Process Metallurgy and Metal Recycling
RWTH Aachen
Prof. Dr.-Ing. Bernd Friedrich
Highly contaminated effluents from RTB Bor, Serbia

Wastewater from Electrolyte-, precious metals and electrolyte regeneration plant

Flow rate:
45 m³/day
(50,000 t Cu/a)
Cu: approx. 8 g/l
pH: 0 - 0.27
### Highly contaminated effluents from RTB Bor, Serbia

**Wastewater from Electrolyte-, precious metals and electrolyte regeneration plant**

<table>
<thead>
<tr>
<th>Concentration, g/dm³</th>
<th>Analytical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8.33</td>
</tr>
<tr>
<td>Ni</td>
<td>0.66</td>
</tr>
<tr>
<td>As</td>
<td>0.63</td>
</tr>
<tr>
<td>Se</td>
<td>0.26</td>
</tr>
<tr>
<td>Fe</td>
<td>0.086</td>
</tr>
<tr>
<td>Sb</td>
<td>0.075</td>
</tr>
<tr>
<td>Te</td>
<td>0.068</td>
</tr>
<tr>
<td>Al</td>
<td>0.04</td>
</tr>
<tr>
<td>Zn</td>
<td>0.034</td>
</tr>
<tr>
<td>Bi</td>
<td>0.028</td>
</tr>
<tr>
<td>Si</td>
<td>0.022</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0034</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0011</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0001</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>120.79</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Flow rate: 45 m³/day
(50.000 t Cu/a)
Cu: approx. 8 g/l
pH: 0 - 0.27
Main aims

- electrochemical pre-treatment of highly contaminated and strong acidic industrial wastewaters
- applying a continuous technology with high specific surface area - using of rotating disc cathodes
- metallic recovery of copper as powder product
- determination of best process operation conditions regarding metal deposition rate as well as solution and metal purity
- optimized current density to avoid the formation of arsine – safety issue
Concept of Metal Removal

- Wastewater
- Electrolytic treatment with rotating discs
- Continuous precipitation
- Purified wastewater
Theoretical Background of Electrolytical Treatment
Challenges of electrolytic treatment of As-solutions

Joint deposition of other metals (Se, As, Sb,..) with Cu:

Cathode: \( \text{Cu}^{2+} + 2e^- = \text{Cu} \)
Competing cathode reaction: \( 2 \text{H}^+ + 2e^- = \text{H}_2 \)
Anode: \( \text{H}_2\text{O} = 2 \text{H}^+ + \frac{1}{2} \text{O}_2 + 2e^- \)

Formation of highly toxic AsH\(_3\) (ARSINE) and SbH\(_3\) (STIBINE)

\( 2 \text{As}^{3+} + 3\text{H}_2 = 2 \text{AsH}_3 + 6 \text{e}^- \)
\( 2 \text{Sb}^{3+} + 3\text{H}_2 = 2 \text{SbH}_3 + 6 \text{e}^- \)

Prevention of AsH\(_3\)-formation by FeAsO\(_4\)-deposition or by avoiding hydrogen formation (optimized current density)

\( \text{Fe}^{2+} - \text{e}^- = \text{Fe}^{3+} \quad \text{and} \quad \text{As}^{3+} - 2\text{e}^- = \text{As}^{5+} \)
\( \text{Fe}^{3+} + 2 \text{O}_2 + \text{As}^{5+} = \text{FeAsO}_4 + 8 \text{e}^- \)
Electrolytic Treatment – Experimental Setup

Technical data of the electrolytic cell:

- cell length/width/height: 34/13/20 cm
- working cell volume: 3l (both cells)
- cathode type: stainless steel discs
- cathode diameter: 30 cm
- total immersed cathode area: 940 cm²
- two cathode discs parallel
- anode type: basket with titanium grid
- basket length/width/height: 30/2,5/15 cm
- electrolyte flow:
  - a) from cell to cell
  - b) through basket to cathode
Electrolytic treatment – Experimental Parameters

**Parameters:**
- Temperature: 20-22°C
- Deposition time: 5, 10 and 20 h
- Average cell voltage: 2.3 V
- Current density: 50 – 80 - 100 A/m²
- Current: 4.7 - 7.5 – 9.9 A
- Cathode revolutions: 2 rpm
- Flow rate: 0.5 - 1.0 - 2.0 l/h
- Active surface: 0.094 m²
- C-c distance: 30 mm
- C-a distance: 15 mm
## Electrolytic treatment - Experimental part

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>current density (A/m²)</th>
<th>Volume flow (l/h)</th>
<th>solution type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>240</td>
<td>0.5</td>
<td>Synthetic</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>0.5</td>
<td>Synthetic</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>0.5</td>
<td>Synthetic</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>1.0</td>
<td>Synthetic</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>2.0</td>
<td>Synthetic</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>0.5</td>
<td>Real</td>
</tr>
<tr>
<td>7</td>
<td>80</td>
<td>0.5</td>
<td>Real</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>0.5</td>
<td>Real</td>
</tr>
<tr>
<td>9</td>
<td>80</td>
<td>1.0</td>
<td>Real</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
<td>2.0</td>
<td>Real</td>
</tr>
</tbody>
</table>
Electrolytic treatment - Results (deposition)

**synthetic wastewater**
- fine layer of powder

**real wastewater**
- black powder directly after test start
- a dark reddish gray deposition after 60 min
• change of current density from 50 A/m² to 100 A/m² increases the metal removal for Cu, As, Te

• metal removal of Se is always high

• in case of Zn the current density has no influence
Electrolytic treatment - Results (current density)

<table>
<thead>
<tr>
<th>current density (A/m²)</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Start</td>
<td>8330</td>
</tr>
<tr>
<td>50</td>
<td>3790</td>
</tr>
<tr>
<td>80</td>
<td>478</td>
</tr>
<tr>
<td>100</td>
<td>308</td>
</tr>
</tbody>
</table>

Electrolytic treatment alone can not ensure metal concentration in the allowed values.
Electrolytic treatment - Results (flow rate)

<table>
<thead>
<tr>
<th>content (g/l)</th>
<th>Initial</th>
<th>0.5 l/h</th>
<th>1.0 l/h</th>
<th>2.0 l/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8.33</td>
<td>0.478</td>
<td>2.86</td>
<td>3.54</td>
</tr>
<tr>
<td>As</td>
<td>0.63</td>
<td>0.063</td>
<td>0.49</td>
<td>0.52</td>
</tr>
<tr>
<td>Se</td>
<td>0.26</td>
<td>0.005</td>
<td>0.0613</td>
<td>0.0862</td>
</tr>
<tr>
<td>Zn</td>
<td>0.034</td>
<td>0.0312</td>
<td>0.032</td>
<td>0.0337</td>
</tr>
</tbody>
</table>

Best results of metal removal obtained for 0.5 l/h
Electrolytic treatment - ICP, SEM and EDX Analysis

Typical EDX Analysis from the powder deposit

ICP analysis of powder composite in %:

80 Cu, 4 As, 3 Se, 0.6 Te, 0.4 Sb, 0.2 Bi,
0.2 Si, 0.1 Zn, 0.02 Pb, <0.01 Al, Ni, Mn, Cd
Conclusions

• Copper was deposited with removal efficiencies of >95% from wastewater with 8.3 g/l Cu and 120.8 g/l H$_2$SO$_4$ in a continuous electrolytic cell with rotating discs at room temperature

• suitable operation parameters are 0.5 l/hour (flow rate) and 100 A/m$^2$ (current density) due to safety reasons

• current efficiency for 100 A/m$^2$ is 58 %

• electrolytic treatment alone can not ensure the legally prescribed metal concentration requirements

Next steps:
• used of platined titanium instead of stainless steel
• improving of the collection method
Thank you for your attention

The authors gratefully acknowledge the financial support of the European Commission for the Research Project INTREAT (INCO-CT-2003-509167), within the Sixth Framework Programme for Research and Development.

IME Process Metallurgy and Metal Recycling
RWTH Aachen University, Germany
Prof. Dr.-Ing. Bernd Friedrich
Existing Technologies for electrolytic WW-treatment

Two companies offer rotating cylinder electrode technology:
1. Electrometals Electrowinning EMEW® Cell - Australia
2. “Elektrolyse und Umweltschutz” Eilenburg

The electrolyte is circulated rapidly past the anode and cathode at a higher flow rate, allowing for improvements in efficiency and recovery. The electrolyte is pumped through the cell from the bottom.