Improved (bio) processing methods for complex ore, Lubin black shale case study

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IMN, Non-ferrous metals Research Institute, Poland
Context of the study

> **Cu and Ag concentrate**
  
  • Black Shale Ore deposit (KGHM, Lubin, Poland)
  • Carbonate-rich
  • Polymineral: chalcocite, bornite, covellite, chalcopyrite
  • Flotation indexes
    — Always been poor
    — in last 5-6 years further degradation (Cu ↓ As ↑)

> **Pyrometallurgical process currently applied**
Context of the study

> Bioleaching demonstrated to be a viable option
  - Testwork at 42°C in batch and continuous mode
  - Cu recovery > 95% in batch mode (10% solids)
  - Cu recovery limited in continuous mode to 92% (15% solids, 6.5 days residence time)
    - Partial chalcopyrite oxidation

> Preliminary techno-economic study

Potential economic feasibility (Spolaore et al. 2009)

Aim of this work: Improve profitability of the process and demonstrate the advantage of bioprocessing route
How to improve process economy?

- **Process economy improvement**
  - **↑ revenues by improving process efficiency**
  - **↓ operating costs**
  - **↓ capital costs**
    - = **↓ tank volume**
    - **↓ Eh (< 420 mV)**
    - **better dissolution of chalcopyrite**
    - **↓ Agitation / aeration rates**
    - **Direct electrowinning**
      - **→ high Cu content**
    - **↑ solids feed content > 20%**
    - **↓ residence time < 6.5 days**

Cordoba et al. 2008; Pinches et al. 2000; Third et al 2002; Tshilombo et al 2002

**Non-traditional operating conditions:**
- Bioleaching tests (BRGM)
- Electrowinning tests (IMN)
Materials and methods: bioleaching tests

### Conditions investigated:
- ↓ agitation/aeration rates to ↓ Eh
- ↑ solids concentration to 25%

### Nutritive medium
- 0Km/3

### Analytical techniques:
- pH, Eh, DO, OUR
- [Cu - Fe]
- bacterial community structure (CE-SSCP)

### Initial operating conditions:
- 42°C, residence time 4.5 days, pH < 2, non-limiting oxygen transfer + 1% CO₂

### Cu concentrate (%)

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>As</th>
<th>Cmin</th>
<th>Corg</th>
<th>Cu</th>
<th>Fe</th>
<th>S=</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.09</td>
<td>0.1</td>
<td>1.9</td>
<td>8.2</td>
<td>14.6</td>
<td>7.5</td>
<td>15.9</td>
</tr>
</tbody>
</table>

### Bacterial consortium
- Leptospirillum, Acidithiobacillus, and Sulfobacillus

### Nutritive medium
- H₂SO₄ (20% v/v)
Results: bioleaching tests

20% solids feed concentration

Non limiting O₂ transfer

<table>
<thead>
<tr>
<th>Concentrate and nutrients</th>
<th>H₂SO₄ (20% v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50L</td>
<td></td>
</tr>
</tbody>
</table>

| pH           | 1.6            |
| Eh (mV)      | 600            |
| O₂ (mg/L)    | 5.6            |
| OUR (mg/L/h) | 193            |

63% Cu dissolution in 5.2 days
Results: bioleaching tests

20% solids + ↓ agitation/aeration rates in R1

- 800 to 100 L/h
- 450 to 340 rpm

Concentrate and nutrients

H₂SO₄ (20% v/v)

50L

20L

20L

pH 1.8
Eh (mV) 592
O₂ (mg/L) 3.2
OUR (mg/L/h) 86

Concentrate

and nutrients

H₂SO₄

(20% v/v)

20% solids

20% solids aeration/agitation R1

No Eh ↓ but Cu dissolution ↑
74% Cu recovery in 4.7 days
Results: bioleaching tests

25% solids + ↓ AAR in R2 and R3

- 400 to 50 L/h
- 420 to 300 rpm

Concentrate and nutrients

H₂SO₄ (20% v/v)

50L

20L

20L

20% solids aeration/agitation R1

25% solids agitation/aeration R1/2/3

pH 1.3
Eh (mV) 601
O₂ (mg/L) 1.9
OUR (mg/L/h) 115

87% Cu recovery in 4.5 days
Results: bioleaching tests

Structure of the bioleaching consortium
• At the end of batch, Bioshale-BRGM species present
• In continuous mode, gradual ↓ of diversity
• Finally, 2 organisms: *Sb. benefaciens* and *L. ferriphilum*

![Bar chart showing the ratio of organisms over time in different conditions.]

All functions still present
Materials and methods: direct electrowinning tests

Pregnant Leach Solution

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>As</th>
<th>Cl</th>
<th>Zn</th>
<th>Cu</th>
<th>Fe</th>
<th>Fe²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt; 0,0002</td>
<td>0.24</td>
<td>0.46</td>
<td>2.99</td>
<td>44.9</td>
<td>5.76</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Pre-treatment tests:

- Hydrolytic Fe(III) removal using calcium carbonate
- Fe(III) removal by jarosite precipitation combined to Cl-removal

Continuous EW tests for Cu removal:

- Constant Cu²⁺ content (~ 30 g/L)
- Temperature: 55 °C
- Cathode current density: 200 A/m²
- Residence time in the cell: 1h

Continuous monitoring of:

- Current intensity,
- bath voltage,
- current efficiency
- electrical energy consumption

→ Comparison with SX-EW tests
Results: direct EW tests

<table>
<thead>
<tr>
<th>Fe(III) removal tests</th>
<th>Initial solution (g.dm⁻³)</th>
<th>Mass of precipitated residue (g)</th>
<th>Final solution (g.dm⁻³)</th>
<th>Removal to residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu²⁺</td>
<td>Fe</td>
<td>Cu²⁺</td>
<td>Fe</td>
</tr>
<tr>
<td>Hydrolytic Fe(III) removal using calcium carbonate</td>
<td>44,91</td>
<td>5,76</td>
<td>161,8</td>
<td></td>
</tr>
<tr>
<td>Fe(III) removal by jarosite precipitation</td>
<td>44,91</td>
<td>5,76</td>
<td>51,9</td>
<td></td>
</tr>
</tbody>
</table>

Hydrolytic removal: 96% of Fe(III) removed but significant loss of copper due to difficulties in filtration of the precipitate.

Jarosite precipitation: 71% of Fe(III) removed but lower loss of copper (easier filtration of the precipitate).
Results: direct EW tests

<table>
<thead>
<tr>
<th>Initial solution</th>
<th>Mass of copper cathode (g)</th>
<th>Current efficiency (%)</th>
<th>Energy consumption (kWh/t Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no pre-treatment</td>
<td>133.8</td>
<td>70.35</td>
<td>2653</td>
</tr>
<tr>
<td>hydrolytic Fe(III) removal</td>
<td>106.3</td>
<td>95.72</td>
<td>1828</td>
</tr>
<tr>
<td>Fe(III) removal by jarosite precipitation</td>
<td>97.6</td>
<td>91.06</td>
<td>2055</td>
</tr>
<tr>
<td>Fe(III) removal by jarosite precipitation combined to Cl- removal</td>
<td>90.8</td>
<td>91.47</td>
<td>2012</td>
</tr>
</tbody>
</table>

Fe(III) removal: ↓ energy consumption  
Cl removal: ↓ dendritic accretions onto copper deposits

<table>
<thead>
<tr>
<th>ppm</th>
<th>Ag</th>
<th>Pb</th>
<th>Fe</th>
<th>Zn</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impurities in the cathode</td>
<td>11,3</td>
<td>1,2</td>
<td>&lt;1</td>
<td>2,8</td>
<td>&lt;0,1</td>
</tr>
<tr>
<td>Max</td>
<td>25</td>
<td>5</td>
<td>10</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>
Conclusions

> Initial objectives
  • Improve profitability of Cu concentrate bioleaching
  • Test of non traditional operating conditions

> Bioleaching step:
  • Technical 25% solids feasibility demonstrated
  • Improvement of Cu dissolution when ↓ agitation/aeration rates

> EW steps:
  • Direct EW works!
  • Cu cathode of proper quality (morphology and composition) at industrial current densities
  • Good current efficiency (90 – 95 %) and power consumption (~2000 kWh/tCu), even with high Mg, Zn, Ni, Co, As concentrations in the electrolytes
  • Conditions: Fe(III) <2g/L, Cl <0.5 g/L

87% Cu dissolution in 4.5 days BUT 25% instead of 15% in previous tests
Lubin concentrate

Mg, Ca, Cl leaching

Gypsum flotation

Gypsum disposal

Residue-treatment

Bioleaching

Jarosite precipitation

Jarosite disposal

Electrowinning

Cu liberation

Cu cathodes

Evaporation & crystallization

Mix-sulphates (Zn, Co, Ni, Cu, Fe, Mg)

Gypsum precipitation

Gypsum to ETP

Mix-sulphates (Zn, Co, Ni, Cu, Fe, Mg)

External H$_2$SO$_4$

→ Ag recovery (tested by IMN)

→ Economic evaluation (handled by CUPRUM)