COPPER AND ZINC RECOVERIES AND ARSENIC STABILIZATION FROM COPPER SMELTER FLUE DUSTS

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In previous works, we have developed some processes for copper and zinc recovery and arsenic stabilization, from copper smelter flue dusts materials, at laboratory scale.

The proposed processes are based on the following items:

• Hydrometallurgical process using dilute reagents
• Operating at room temperature and atmospheric pressure
• With few unit operations and low energy costs
• Generation of final compact and inert residue for landfill.

The objective of the present work is the description of two possible routes for the treatment of copper smelter flue dust samples, including the study of copper and zinc recovery from the leaching liquors using processes such as cementation and electrolysis, in the presence of arsenic in solution.
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From previous work:

• The leaching processes can be carried out leaching with water or dilute sulphuric acid (high amounts of copper are present in the dusts as copper sulphate and basic sulphate).

• If residual sulphides are present the residue obtained after leaching can be hydro-cycloned being the coarse fraction (including sulphides and ferrites), recycled to the furnace and the fine fraction (arsenic-rich fraction), should be mixed with wastewater sludge from a paper factory, to make both residues inert before landfill them.

• When residual sulphides are not present (dusts from flash furnace), the residue obtained after leaching with sulphuric acid is subjected to the same treatment as the arsenic-rich fraction described above.
Characterization of copper smelter flue dusts

Chemical composition (range) of copper smelter flue dusts. [XRF]

<table>
<thead>
<tr>
<th>Element</th>
<th>wt%</th>
<th>Element</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>26 – 37</td>
<td>Si</td>
<td>1.1 - 1.7</td>
</tr>
<tr>
<td>Fe</td>
<td>11 – 14</td>
<td>Cd</td>
<td>0.12 - 0.66</td>
</tr>
<tr>
<td>As</td>
<td>3.8 – 13</td>
<td>Pb</td>
<td>0.43 - 5.1</td>
</tr>
<tr>
<td>Zn</td>
<td>4.5 - 5.8</td>
<td>Mo</td>
<td>0.40 - 0.64</td>
</tr>
<tr>
<td>S</td>
<td>5.6 - 6.5</td>
<td>Bi</td>
<td>0.13 - 1.1</td>
</tr>
</tbody>
</table>
Characterization of copper smelter flue dusts

The main phases:
- spinel phases (from magnetite to cuprospinel),
- copper sulphate (chalcocianite),
- copper basic sulphate (dolerofanite),
- zinc sulphate (zinkosite) and
- in some cases arsenic oxides (claudetite and arsenolite)

The minor phases:
- copper oxides (cuprite and tenorite) and
- copper iron oxide (delafossite)

Samples from continuous furnaces:
- copper sulphides and
- sulphoarsenides: digenite, anilite, bornite, cubanite and enargite.

[XRD]
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Characterization of copper smelter flue dusts
SEM-SE images of a copper smelter flue dust sample
COPPER AND ZINC RECOVERIES AND ARSENIC STABILIZATION FROM COPPER SMELTER FLUE DUSTS

Characterization of copper smelter flue dusts

SEM-BSE images of a copper Smelter flue dust sample

EDS diagrams of a copper sulphate (1) and a cuprospinel phase (2)

EDS diagrams of oxides of copper and arsenic (3) and oxide of copper (4)
COPPER AND ZINC RECOVERIES AND ARSENIC STABILIZATION
FROM COPPER SMELTER FLUE DUSTS

Leaching of copper smelter flue dusts with sulphuric acid solutions

The sulphuric acid solution : 0.1 M
Solid-liquid : 1/5 (w/v)
Temperature : at room temperature
pH : initial : 1.3; final : 1.40

Distribution of copper, iron, zinc, arsenic and sulphur after leaching:

<table>
<thead>
<tr>
<th>Element (%)</th>
<th>Cu</th>
<th>Fe</th>
<th>Zn</th>
<th>As</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>In residue</td>
<td>68</td>
<td>91</td>
<td>10</td>
<td>30</td>
<td>23</td>
</tr>
<tr>
<td>In solution</td>
<td>32</td>
<td>9</td>
<td>90</td>
<td>70</td>
<td>77</td>
</tr>
</tbody>
</table>

Residue from leaching:
coarse fraction (> 12 μm) : 46% Cu, 22% Fe, 0.19% Zn, 0.06% As
fine fraction : 17% Cu, 25% Fe, 1.4% Zn, 11% As
Iron arsenate precipitation

The filtrate was injected with ozone:

to oxidise the remaining arsenic (III) to As (V) and
then was heated at 80 ºC to promote the precipitation of arsenic as iron arsenate.

The pH of liquids after precipitation was 1.35

Analysis precipitate: [EDS]

the main elements: arsenic and iron;
the minor elements: copper and cadmium.

Phases in this precipitate [XRD]: amorphous.

Solid waste: [EPMA]

Fe: 20-22%,
As: 29%,
Cu: 1.5-3% and
S: 0.25-0.40%.
Iron arsenate precipitation

Chemical composition of leach solution after iron arsenate separation [ICP]:

<table>
<thead>
<tr>
<th>Cu (g·L⁻¹)</th>
<th>Zn (g·L⁻¹)</th>
<th>S (g·L⁻¹)</th>
<th>Fe (mg·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.6</td>
<td>1.1</td>
<td>8.3</td>
<td>350</td>
</tr>
<tr>
<td>As (mg·L⁻¹)</td>
<td>Cd (mg·L⁻¹)</td>
<td>Mo (mg·L⁻¹)</td>
<td>Ca (mg·L⁻¹)</td>
</tr>
<tr>
<td>550</td>
<td>33</td>
<td>41</td>
<td>163</td>
</tr>
</tbody>
</table>
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Transformation of iron arsenate precipitates to an arsenical natroalunite

Hydrothermal precipitation:
iron arsenate precipitated was mixed with aluminium sulphate and sodium sulphate and introduced in a pressure vessel.

Diffractogram of arsenical natroalunite [XRD]:

Arsenical natroalunite [ICP]:

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>9.4</td>
</tr>
<tr>
<td>Fe</td>
<td>8.8</td>
</tr>
<tr>
<td>S</td>
<td>9.1</td>
</tr>
<tr>
<td>As</td>
<td>11</td>
</tr>
<tr>
<td>Na</td>
<td>2.84</td>
</tr>
</tbody>
</table>
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Copper recovery from the leaching liquid
Cementation:
Iron powder: 16 g∙L\(^{-1}\) (>95% Fe),
Liquid composition after copper cementation at different times: [ICP]

<table>
<thead>
<tr>
<th>Element (mg∙L(^{-1}))</th>
<th>7.5</th>
<th>15</th>
<th>30</th>
<th>60</th>
<th>120</th>
<th>1,440</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>400</td>
<td>140</td>
<td>6.8</td>
<td>2.7</td>
<td>6.6</td>
<td>9.7</td>
</tr>
<tr>
<td>Fe</td>
<td>11,300</td>
<td>11,900</td>
<td>11,800</td>
<td>12,200</td>
<td>12,300</td>
<td>13,600</td>
</tr>
<tr>
<td>Zn</td>
<td>1,060</td>
<td>1,080</td>
<td>1,030</td>
<td>1,050</td>
<td>1,010</td>
<td>1,090</td>
</tr>
<tr>
<td>As</td>
<td>560</td>
<td>520</td>
<td>445</td>
<td>390</td>
<td>300</td>
<td>190</td>
</tr>
<tr>
<td>Mo</td>
<td>34</td>
<td>36</td>
<td>26</td>
<td>21</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td>Cd</td>
<td>27</td>
<td>27</td>
<td>26</td>
<td>26</td>
<td>25</td>
<td>26</td>
</tr>
</tbody>
</table>

Original dissolution: 12.6 g∙L\(^{-1}\) of copper and 0.35 g∙L\(^{-1}\) of iron.
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Copper recovery from the leaching liquid

Cementation:

SEM images

Problems:
- the introduction of high amounts of iron into the solution,
- possible generation of arsine.
Copper recovery from the leaching liquid

Electrolysis:
- potential: 2 V
- current density: 1.2 A·dm$^{-2}$
- copper: > 99% (SEM-EDS)
- current yield: 90%
- electrolyte:
  - final pH: 0.70,
  - copper concentration: 12.6 g·L$^{-1}$ $\rightarrow$ 1.0 g·L$^{-1}$ in 8 hours.
COPPER AND ZINC RECOVERIES AND ARSENIC STABILIZATION FROM COPPER SMELTER FLUE DUSTS

Copper recovery from the leaching liquid

Electrolysis:

Percent recovery of copper vs time during the electrolytic process.

![Graph showing copper recovery vs time]

- final electrolyte: recycled to the leaching step (to increase zinc concentration);
- drained in a percentage to recover zinc by electrolysis or by chemical precipitation.
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PROCESS FOR THE TREATMENT OF COPPER SMELTER FLUE DUSTS

Pellet : (Test DIN 38414-S4)
Chemical composition of the leach solution (mg·L⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Fe</th>
<th>As</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet</td>
<td>45</td>
<td>0.4</td>
<td>&lt; 5</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>0.74</td>
<td>0.3</td>
<td>0.3</td>
<td>0.13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Cd</th>
<th>Ni</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet</td>
<td>3.2</td>
<td>2.1</td>
<td>&lt; 0.1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td></td>
<td>&lt; 0.2</td>
<td>&lt; 0.1</td>
<td>&lt; 0.01</td>
<td></td>
</tr>
</tbody>
</table>
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PROCESS FOR THE TREATMENT OF COPPER SMELTER FLUE DUSTS

Precipitation to iron arsenate:
- ozone
- aluminium sulphate: 1 kg per kg of copper smelter flue dusts
- sodium sulphate: 0.2 kg per kg of copper smelter flue dusts.
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PROCESS FOR THE TREATMENT OF COPPER SMELTER FLUE DUSTS

Copper and Zinc recovery:

\[ \text{Dusts} \rightarrow \text{Leaching} \rightarrow \text{Filtrate} \rightarrow \text{Iron Arsenate Precipitation} \rightarrow \text{S/L Separation} \rightarrow \text{Electrolysis} \rightarrow \text{Cu, Drain off} \rightarrow \text{Zn Recovery} \]
COPPER AND ZINC RECOVERIES AND ARSENIC STABILIZATION FROM COPPER SMELTER FLUE DUSTS

PROCESS FOR THE TREATMENT OF COPPER SMELTER FLUE DUSTS

[Diagram showing the process flow for treating copper smelter flue dusts, including leaching, precipitation, electrolysis, and other steps leading to Zn recovery and Cu extraction.]