MANAGEMENT OF A COPPER SMELTER DUST FOR COPPER PROFIABILITY

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Copper production by pyrometallurgical processing is nowadays an important part of the metallurgy industry.

Copper dusts production is inherent with all the furnace types used in pyrometallurgy.

Copper dusts are defined as the product recovered from exhaust gas streams found in furnace, flues, and setting chambers as a result of roasting, smelting, and converting operations from copper refining process.
Due to its physical and chemical characteristics, these copper dusts were categorized as hazardous wastes.

These residues must be stored in specialized landfills.

Due their important amount of various form of copper compounds (even metallic copper) could be used as secondary raw material in the production of this metal.

Pyrometallurgy

Hydrometallurgy

Several processes have the main idea the leaching with ammonium salts

Copper is stabilized in the aqueous solution as the corresponding ammine-copper complexes

The solutions are practically free of non-desired elements, remaining in the solid residue due to the alkalinity of the solutions.
A sequential process of a Chilean copper flue dust is given based in:

i) leaching with ammonium carbonate solution

ii a) cementation of copper from the solution using metallic zinc. Copper cement is the final product

ii b) liquid-liquid extraction of copper using LIX 54 as extractant and sulphuric acid as strippant. The final product could be copper cathode
EXPERIMENTAL

Materials

Dust from the flash furnace Chilean copper smelting plant

<table>
<thead>
<tr>
<th>XRD Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcocyanite</td>
</tr>
<tr>
<td>CuSO₄</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical Characterization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>24.5</td>
</tr>
</tbody>
</table>
i) Leaching
   - Mild conditions - Reduce energy costs

   ii a) Cementation
      - Stirring speed: 300 min\(^{-1}\)
      - Glass reactor- impeller
      - Continuous conditions
      - Water jacketed (100 ml) separatory funnels
      - Mechanical shaking and thermostated (20°C)

   ii b) Solvent extraction
      - Batch conditions
      - Mechanical shaking and thermostated (20°C)
      - Continuous conditions
      - Water jacketed mixer-settler
      - Mechanical shaking and thermostated
Extraction agent \[ \text{LIX 54 (\(\beta\)-diketone)} \]

\[ \text{R-CO-CH}_2\text{-CO-R'} \]

\[ \text{R y R’- Alkyl chains} \]

<table>
<thead>
<tr>
<th>Property</th>
<th>Kerosene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic</td>
<td>98%</td>
</tr>
<tr>
<td>Boiling range</td>
<td>210-284°C</td>
</tr>
<tr>
<td>Flash point</td>
<td>96°C</td>
</tr>
</tbody>
</table>
i) LEACHING

Leaching reagent:

a) It must dissolve the targeted metal as rapidly as possible to make commercially feasible the operation, and it should no attack the non-desiderable elements or gange of the initial material

\[(\text{NH}_4\text{)}_2\text{CO}_3\]

b) It must be cheap

b) It is better that it can be regenerated within the whole process
RESULTS

i) LEACHING

Ammonium carbonate concentration no affect on leaching cooper percentage

<table>
<thead>
<tr>
<th>(NH₄)₂CO₃ (g/L)</th>
<th>L/S ratio</th>
<th>pH</th>
<th>%Cu leached</th>
<th>Cu in solution (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>100</td>
<td>8.6</td>
<td>79.6</td>
<td>1.95</td>
</tr>
<tr>
<td>130</td>
<td>100</td>
<td>8.7</td>
<td>82.4</td>
<td>2.02</td>
</tr>
<tr>
<td>65</td>
<td>100</td>
<td>8.7</td>
<td>81.2</td>
<td>1.99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(NH₄)₂CO₃ (g/L)</th>
<th>L/S ratio</th>
<th>pH</th>
<th>%Cu leached</th>
<th>Cu in solution (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>100</td>
<td>8.5</td>
<td>79.9</td>
<td>19.6</td>
</tr>
<tr>
<td>65</td>
<td>200</td>
<td>8.8</td>
<td>92.2</td>
<td>1.13</td>
</tr>
<tr>
<td>65</td>
<td>100</td>
<td>8.7</td>
<td>81.2</td>
<td>1.99</td>
</tr>
<tr>
<td>65</td>
<td>20</td>
<td>7.8</td>
<td>45.1</td>
<td>5.50</td>
</tr>
<tr>
<td>65</td>
<td>10</td>
<td>7.3</td>
<td>9.8</td>
<td>2.40</td>
</tr>
</tbody>
</table>

L/S ratio no affect in the %Cu leached when concentrated (NH₄)₂CO₃ solution are used

However, the %Cu drops as the initial L/S ratio decrease when the dilute (NH₄)₂CO₃ solution are used

This is due to the decrease of the number of ammonia ligands available per copper atom.
i) LEACHING

Higher copper concentrations can be yield in the solutions after leaching with ammonium carbonate solutions

\[ \text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+ \]

\[ \text{Cu(NH}_3\text{)}_n^{2+} \quad n = 2 \text{ or } 4 \]

Despite the generation of ammonia, the pH of the solution does not vary appreciably since most of the generated ammonia is complexed by copper (II), while the uncomplexed ammonia and the ammonium salts resulting in a buffer system which maintained the pH of the solution almost fixed.

Being this pH slightly alkaline, the leaching solution is very pure, having very low values of other impurities found in the flue dust and free of iron, which remained in the residue probably as an iron (III) oxide species.
The pH is slightly alkaline, the solution obtained from the leaching operation is very pure, having very low values (in the range of few mg/L) of other impurities found in the flue dust and free of iron, which remained in the residue probably as an iron (III) oxide species.
ii a) CEMENTATION

The cementation of copper from an alkaline solution was done by metallic zinc, according with the overall reaction

\[ \text{Cu}^{2+} + \text{Zn}^0 \rightarrow \text{Cu}^0 + \text{Zn}^{2+} \]

\[ \frac{\text{Cu}^{2+}/\text{Cu}^0}{\text{Cu}^{2+}/\text{Cu}^0} = 0.34 \]  
\[ \Delta G_{298}^0 = -35.19 -15.54 = -50.73 \text{ Kcal} \]

\[ \frac{\text{Zn}^{2+}/\text{Zn}^0}{\text{Zn}^{2+}/\text{Zn}^0} = -0.76 \]
Results

ii a) CEMENTATION: pH effect

Cu$^{2+}$ is well cementated at pH=4 but bad precipitated form ammonical alkaline solution.

This situation can be remediated if the aqueous solution contain an excess of ammonia ligands and the pH is maintained in 8-9 range.
ii a) CEMENTATION: metal concentration

At the end, the molar relationship $\frac{\text{Zn}^{2+}_{(\text{liq})}}{\text{Cu}^0_{(\text{sol})}} \approx 1$

$\text{Cu}^{2+} + \text{Zn}^0 \rightarrow \text{Cu}^0 + \text{Zn}^{2+}$
### ii a) CEMENTATION: salt addition

<table>
<thead>
<tr>
<th>(NH$_4$)$_2$CO$_3$ (g/L)</th>
<th>15 min</th>
<th>30 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>13.1</td>
<td>13.3</td>
<td>13.5</td>
</tr>
<tr>
<td>89</td>
<td>34.5</td>
<td>46.4</td>
<td>44.7</td>
</tr>
<tr>
<td>113</td>
<td>65.0</td>
<td>86.8</td>
<td>97.4</td>
</tr>
<tr>
<td>160</td>
<td>91.0</td>
<td>99.1</td>
<td>&gt;99.5</td>
</tr>
<tr>
<td>210</td>
<td>65.2</td>
<td>91.8</td>
<td>&gt;99.5</td>
</tr>
<tr>
<td>260</td>
<td>68.5</td>
<td>87.5</td>
<td>&gt;99.5</td>
</tr>
</tbody>
</table>

Aqueous solution: 10 g/L Cu$^{2+}$ in (NH$_4$)$_2$CO$_3$, pH 8.5 ±0.02  
Zn/Cu molar ratio: 2  
Temperature: 20ºC

The salt addition, ammonium carbonate, increases the copper cementation percentage.
### ii a) CEMENTATION: influence Zn/Cu ratio

<table>
<thead>
<tr>
<th>Zn/Cu</th>
<th>15 min</th>
<th>30 min</th>
<th>60 min</th>
<th>2 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>84.2</td>
<td>95.0</td>
<td>99.5</td>
<td>&gt;99.5</td>
</tr>
<tr>
<td>6</td>
<td>53.2</td>
<td>63.6</td>
<td>80.5</td>
<td>98,3</td>
</tr>
<tr>
<td>4</td>
<td>48.5</td>
<td>61.1</td>
<td>73.0</td>
<td>97,6</td>
</tr>
</tbody>
</table>

Aqueous solution: 5 g/L Cu$^{2+}$ and 65 g/L (NH$_4$)$_2$CO$_3$, pH 8.5 ±0.02, Temperature: 20ºC

Zn/Cu molar ratio increased a increases the Cu$^{2+}$ percentage cementated.

The same tendency is observed to a concentration of ammonium carbonate 260 g/L. The maximum percentage of copper cementated is obtained to 1.5 Zn/Cu ratio.
ii a) CEMENTATION: cement morphology

Aqueous solution: 5 g/L Cu$^{2+}$ and 160 g/L (NH$_4$)$_2$CO$_3$, pH 4.0 ±0.02
Temperature: 20ºC

Aqueous solution: 5 g/L Cu$^{2+}$ and 160 g/L (NH$_4$)$_2$CO$_3$, pH 8.5 ±0.02
Temperature: 20ºC

The copper cementated has the form of granular particles. The unreacted zinc is represented by the non-granular specimens.
Too much dilute copper (i.e. below 5 g/L) or complex solutions result unpractical for direct production of copper cathodes

Liquid-liquid extraction is the technology which ensures the production of lean copper solution with the adequate concentration to be their direct feeding to the electrowinning plant and to yield a grade A copper cathode.

- First step: Metal extraction
- Second step: Metal stripping from loaded organic solution
RESULTS

**ii b) LIQUID-LIQUID EXTRACTION**

First step: Metal extraction

Liquid-liquid Cu(II) extraction the agent extraction most widely used are:

- Ketoxine
- Salicyaladoximes
- Salicyaladoximes

\[
\text{Cu}^{+2}_{\text{aq}} + 2 \text{HR}_{\text{org}} \rightarrow \text{R}_2\text{Cu}_{\text{org}} + 2 \text{H}^{2+}_{\text{aq}}
\]

\(\beta\)-diketone (LIX 54)

\[
\text{Cu(NH}_3\text{)}_2^{+2}_{\text{aq}} + 2 \text{HR}_{\text{org}} \rightarrow \text{R}_2\text{Cu}_{\text{org}} + 2 \text{NH}_4^+_{\text{aq}}
\]

The extraction of the diammine-copper(II) complex \(\text{Cu(NH}_3\text{)}_2^{+2}_{\text{aq}}\), product of the leaching step, result in the neutralization of the protons released to the aqueous solutions by the agent extraction, and regenerating the leaching reagent.
**ii b) LIQUID-LIQUID EXTRACTION**

Second step: Metal stripping

\[
R_2Cu_{\text{org}} + H_2SO_{4\text{aq}} \rightarrow 2HR_{\text{org}} + Cu^{2+}_{\text{aq}} + SO_4^{2-}_{\text{aq}}
\]

The stripping agent was a H$_2$SO$_4$ solution (i.e. 160-180 g/L H$_2$SO$_4$), this solution represented the advanced electrolyte which feed the electrowinning operation.
ii b) LIQUID-LIQUID EXTRACTION

Preliminary studies

Experiments conditions:

Liquid phase: 2 g/L Cu(II) in 65 g/L (NH$_4$)$_2$CO$_3$ pH 8.5 ± 0.02
Organic phase: 10 %V/V LIX 54 + Kerosene

Equilibrium time= 2.5 min (98.8 %)

Endothermic reaction

First step: Metal extraction

An increase in the ammonium carbonate in the aqueous solution decrease the percentage of copper extraction, from 98.9-80.3 % Cu for ammonium carbonate solutions in 65 to 260 g/L
**RESULTS**

**ii b) LIQUID-LIQUID EXTRACTION**

Preliminary studies

Experiments conditions:

- Liquid phase: 2 g/L Cu(II) in 65 g/L (NH₄)₂CO₃  pH 8.5 ± 0.02
- Organic phase: 10 %V/V LIX 54 + Kerosene

Second step: Metal stripping

The stripping of the metal carried out using spent electrowinning solutions (160-180 g/L H₂SO₄) ensured the strip of the metal from the loaded organic phase to the aqueous solution, which represented the advanced electrolyte
ii b) LIQUID-LIQUID EXTRACTION

Counter-current extraction in mixer-settler unit
- One extraction stage
- Two stripping stage

After 100 h
Copper extraction 99.5%
Copper stripping 99.9%
CONCLUSION

(NH₄)₂CO₃ solution allowed the dissolution of Cu(II) from copper flue dust

\[
\text{CuSO}_4 + (\text{NH}_4)_2\text{CO}_3 \rightarrow \text{Cu(NH}_3)_2^{2+} + \text{SO}_4^{2-} + \text{CO}_3^{2-} + 2\text{H}^+
\]

The metal-lean solution can be processed

ii a) Cementation

\[
\text{Cu}^{2+} + \text{Zn}^0 \rightarrow \text{Cu}^0 + \text{Zn}^{2+}
\]

Cement copper is the final product

ii b) Liquid-liquid extraction

\[
\text{Cu(NH}_3)_2^{2+} \text{aq} + 2 \text{HR}_{\text{org}} \rightarrow R_2\text{Cu}_{\text{org}} + 2 \text{NH}_4^+ \text{aq}
\]

The final product could be copper cathode
THANK YOU FOR YOUR ATTENTION