Recovery of base and precious metals from waste printed circuit boards and spent catalysts by hydrometallurgical processes

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HydroWEE Project

Partners:

1. SAT (Austria)
2. University of L’Aquila (Italia) – Scientific responsible
3. University of Ancona (Italia)
4. University of Roma “La Sapienza”
5. Istituto Pupin (Serbia)
6. Relight Srl (Italia)
7. Greentronics (Romania)
8. SET-trade (Serbia)
HydroWEE Project

- **HydroWEEE (2009-2012).**
  - Development of hydrometallurgical processes for the recovery of precious metals and RE from WEEE

- **HydroWEEE demo (2012-2016) for SME**
  - Realization of two industrial demonstration plants (mobile and stationary) for the hydrometallurgical treatment of WEEE
HydroWEE

Small hydrometallurgical pilot plant
HydroWEEE Demo

Stationary plant

Mobile plant
Initial WPCBs hydrometallurgical process realization

Considering the data achieved within the HydroWEEE project, the experimental tests have been developed to achieve a better sustainability of the procedure with more easily handling operations.

For this reason high importance was given to:

- The methodologies of material preparation (pre-tratament);
- Replacing of the electrowinning procedure with less energy consumption operations;
- Achieving of higher recovery degree with less regents intake;
- Achieving of high purity degree for the outputs.
Brief background on WPCB and their treatments

Categories of WPCB depending on their gold content

- **High grade (>200 ppm)**
  - Mobile phones, ICs, MLCCs

- **Medium grade (100>200 ppm)**
  - PCBs of Laptops, PCs

- **Low grade (<100 ppm)**
  - Boards of TV, monitors, printers etc.

Current methods of treatment

- **Mechanical – Physical Processes**
  - Incomplete separation of elements - pretreatment

- **Pyrometallurgy** - High cost and loss of byproducts in the slag

- **Hydrometallurgy** - Easily control operations

- **Bio-metallurgy** - In the early stage

- **Ionometallurgy** -
Processing of WPCBs within HydroWEEE Demo project

The research activities have been developed considering the following:

- Selective recovery of base metals by the precious ones;
- Promoting of a suitable technology for the residual water;
- Reduction of effluents to zero;
Physical-mechanical pretreatment

Mass balance of the physical treatment
Hydrometallurgical procedures
“Sulfuric acid process: Base metals recovery”

- Two-step counter current leaching:
  - Cu + H\(_2\)SO\(_4\) + H\(_2\)O\(_2\) = CuSO\(_4\) + 2H\(_2\)O
  - Fe + H\(_2\)SO\(_4\) + H\(_2\)O\(_2\) = FeSO\(_4\) + 2H\(_2\)O
  - Zn + H\(_2\)SO\(_4\) + H\(_2\)O\(_2\) = ZnSO\(_4\) + 2H\(_2\)O
  - Ni + H\(_2\)SO\(_4\) + H\(_2\)O\(_2\) = NiSO\(_4\) + 2H\(_2\)O
  - Sn + H\(_2\)SO\(_4\) + H\(_2\)O\(_2\) = SnSO\(_4\) + 2H\(_2\)O

**Experimental conditions:**
- sulfuric acid (1.8M/L)
- hydrogen peroxide (25 % vol./vol.)
- time of treatment 2 h for each step;
- ambient temperature
- solid concentration : 15 % wt./vol.
- agitation rate of 200 rpm

\(\eta_{Cu} = 99\%\)
\(\eta_{Zn} = 100\%\)
\(\eta_{Sn} = 52\%\)
\(\eta_{Fe} = 50\%\)
\(\eta_{Ni} = 100\%\)
Hydrometallurgical procedures
“Sulfuric acid process: Base metals recovery”

**Sn precipitation (Process I)**
For the precipitation of Sn, a flocculant has been used.

Tin precipitation with flocculant at various time periods: a) after 2 minutes; b) after 15 min of polyamine addition; c) after 30 minutes

Tin precipitate and its chemical analysis

Solution after tin precipitation
Copper recovery

Two step countercurrent leaching with sulfuric acid and hydrogen peroxide

Fresh solution
Solid residue

II

I

Final solution
Milled WPCBs

Cementation with Zn

Solid residue

Final solution
Hydrometallurgical procedures
“Sulfuric acid process: Base metals recovery”

**Cu cementation**

For Cu recovery in its metal form, the cementation procedure with zinc metal powder is performed.

- \( \text{CuSO}_4 + \text{Zn}^0 = \text{ZnSO}_4 + \text{Cu}^0 \)

However, due to the very acid character of the solution (pH≤1), a large amount of zinc is consumed and a large amount of hydrogen is produced.

- \( \text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2 \uparrow \)

**Experimental conditions (process I):**

- 50% of Zn excess than the stoichiometric amount;
- 200 rpm for 30 minutes.
Hydrometallurgical procedures

Gold and Silver recovery

Leaching process
The solid residues achieved in both leaching systems of base metals are subjected to thioureation procedure in a two-step cross current manner using the following conditions:

- 10 wt.% solid concentration;
- 20 g/L of CSN2H4;
- 21.4 g/L of Fe2(SO4)3';
- 0.25 M/L H2SO4;
- 200 rpm stirring rate for 90 minutes for each step;
- 2 g/L of CSN2H4 into the second step.

Reactions involved into the system:

- \(2\text{Au} + \text{Fe}_2(\text{SO}_4)_3 + 4\text{SCN}_2\text{H}_4 + \text{SO}^{2-} = [\text{Au}(\text{SCN}_2\text{H}_4)_2]_2\text{SO}_4 + \text{FeSO}_4\)
- \(2\text{Ag} + \text{Fe}_2(\text{SO}_4)_3 + 6\text{SCN}_2\text{H}_4 + \text{SO}^{2-} = [\text{Ag}(\text{SCN}_2\text{H}_4)_3]_2\text{SO}_4 + 2\text{FeSO}_4\)
Hydrometallurgical procedures
Gold and Silver recovery

Cementation process
Experimental conditions:
- Neutralization with NaOH to pH=2
- Zn metal powder considering an amount of 10 times larger than Ag content;
- Room temperature;
- 200 rpm stirring rate for 30 minutes.

Reactions involved within the process:
- \([\text{Au (CS(NH}_2)_2]\text{SO}_4 + \text{Zn} \rightarrow 2\text{Au} + 4\text{CS(NH}_2)_2 + \text{ZnSO}_4]\)
- \([\text{Ag(CS(NH}_2)_3]\text{SO}_4 + \text{Zn} \rightarrow 2\text{Ag} + 6\text{CS(NH}_2)_2 + \text{ZnSO}_4]\)
Gold and silver recovery

Two step cross leaching with thiourea, ferric sulphate and sulphuric acid

1. Fresh solution -> Solution
2. Solution -> Solid residue
3. Solid residue -> Solid residue
4. Solid residue -> Solid residue
5. Solid residue -> Neutralization and Cementation
6. Neutralization and Cementation -> Final solution

Diagram:
- Solid residue
- Fresh solution
- Solution
- Solid residue
- Solid residue
- Final solution
- Neutralization and Cementation

Chart:
- Au, 9.45%
- Ag, 7.88%
- Cu, 7.01%
- Zn, 75%
Hydrometallurgical procedures

Waste water treatment

Residual thiourea solution treatment

During the thiourea leaching procedure, under the action of Fe$^{3+}$, the following irreversible reaction is produced:

- $2\text{SCN}_2\text{H}_4 = (\text{SC}(\text{NH})(\text{NH}_2))_2 + 2\text{H}^+ + 2\text{e}^-$

The formed FDS is afterwards decomposed to thiourea and sulfinic compound which further decompose into cyanamide and elemental sulfur.

- $(\text{SC}(\text{NH})(\text{NH}_2))_2 = \text{SC N}_2\text{H}_4 + \text{NH}_2(\text{NH})\text{CSOOH}$
- $\text{NH}_2(\text{NH})\text{CSOOH}= \text{S}_0 + \text{CN}_2\text{H}_2$

The cyanamide decompose to urea in acid media and the sulfur is oxidized to sulphate

To ensure the complete degradation of the thiourea, the Fenton procedure has been successfully applied. This procedure is followed by the neutralization process with lime for impurities removal.
Hydrometallurgical procedures

Waste water treatment

The reactions of Fenton process are expressed in the following two equations.

- \( \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH} \)
- \( \text{OH}^- + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{Fe}^{3+} \)
- \( 2\text{OH}^- + \text{CS(NH}_2\text{)}_2 = \text{CH}_4\text{N}_2\text{O} + \text{S} + \text{H}_2\text{O} \)

Reactions during the neutralization with lime:

- \( \text{Fe}_2(\text{SO}_4)_3 + 3\text{Ca(OH)}_2 = 2\text{Fe(OH)}_3 + 3\text{Ca(SO}_4) \)
- \( \text{ZnSO}_4 + \text{Ca(OH)}_2 = \text{Zn(OH)}_2 + \text{CaSO}_4 \)
## Wastewater treatment

### Fenton process and neutralization with lime

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit of measure</th>
<th>Initial conditions</th>
<th>After Fenton treat.</th>
<th>Final treatment</th>
<th>Consumption of reagents</th>
<th>Leg. It.</th>
<th>Leg. SrB.</th>
<th>Leg. Ro.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>With NaOH</td>
<td>With Ca(OH)₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>3</td>
<td>1.9</td>
<td>9.3</td>
<td>8.04</td>
<td>5.5-9.5</td>
<td>6.5-9.5</td>
<td>6.5-9.5</td>
</tr>
<tr>
<td>TDS</td>
<td>g/L</td>
<td>96</td>
<td>95.66</td>
<td>109.71</td>
<td>37.16</td>
<td></td>
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</tr>
<tr>
<td>SST</td>
<td>g/L</td>
<td>0.68</td>
<td>1.52</td>
<td>30.92</td>
<td>90.93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>13580</td>
<td>379</td>
<td>258</td>
<td>188</td>
<td>500</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Abatement of COD</td>
<td>%</td>
<td></td>
<td></td>
<td>95.62</td>
<td>96.84</td>
<td>97.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>g/L</td>
<td>41.8</td>
<td>85.46</td>
<td>83.15</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeSO₄</td>
<td>kg/m³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O₂</td>
<td>kg/m³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>kg/m³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>Kg/m³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.76</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Process flow diagram for the application a the industrial level
Economic analysis of the WPCB process

**Costs of reagents:** 14.87 €/t

<table>
<thead>
<tr>
<th>Costs</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2SO4</td>
<td>49%</td>
</tr>
<tr>
<td>H2O</td>
<td>49%</td>
</tr>
<tr>
<td>CS(NH2)2</td>
<td>6%</td>
</tr>
<tr>
<td>Zn</td>
<td>5%</td>
</tr>
<tr>
<td>NaOH</td>
<td>2%</td>
</tr>
<tr>
<td>Ca(OH)2</td>
<td>10%</td>
</tr>
<tr>
<td>FeSO4</td>
<td>0%</td>
</tr>
<tr>
<td>Fe2(SO4)3</td>
<td>1%</td>
</tr>
<tr>
<td>Na2CO3</td>
<td>20%</td>
</tr>
<tr>
<td>Milling</td>
<td>1%</td>
</tr>
<tr>
<td>Disposal WW treat residue</td>
<td>2%</td>
</tr>
<tr>
<td>Personnel</td>
<td>19%</td>
</tr>
<tr>
<td>Plant cost</td>
<td>18%</td>
</tr>
<tr>
<td>Energy consumption</td>
<td>6%</td>
</tr>
<tr>
<td>Raw materials</td>
<td>54%</td>
</tr>
</tbody>
</table>

**Total cost:** 2412 €/t

**Revenue**

<table>
<thead>
<tr>
<th>Product</th>
<th>Price per Kg</th>
<th>Production kg/t</th>
<th>Income per t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>5.87</td>
<td>195</td>
<td>935.92</td>
</tr>
<tr>
<td>Au</td>
<td>38,522.34</td>
<td>0.2646</td>
<td>8,358.27</td>
</tr>
<tr>
<td>Ag</td>
<td>698.01</td>
<td>0.220</td>
<td>125.92</td>
</tr>
<tr>
<td>ZnCO3</td>
<td>1</td>
<td>390</td>
<td>319.60</td>
</tr>
<tr>
<td>SnO2</td>
<td>56.00</td>
<td>19.49</td>
<td>894.82</td>
</tr>
<tr>
<td>Al</td>
<td>1.23</td>
<td>30.41</td>
<td>30.67</td>
</tr>
<tr>
<td>Steel</td>
<td>0.23</td>
<td>23.63</td>
<td>4.46</td>
</tr>
<tr>
<td>Nb2O5</td>
<td>250</td>
<td>0.54</td>
<td>110.49</td>
</tr>
<tr>
<td>Ta2O5</td>
<td>250</td>
<td>0.49</td>
<td>101.28</td>
</tr>
</tbody>
</table>

**Total revenue** 10,634.52 €

**NPV 20% positive**

**PBT = 2.5-3.0 years**

**Price of WPCB = 4.000 €/t**
Hydrometallurgical processing of spent catalysts

Hydrometallurgical process for recovery of lanthanum and cerium by selective precipitation

% Recoveries 70-80%

Spent automotive catalyst

Leaching with HCl+H2O2+NaClO

60 mg/L Pt

Research in progress
What we learned from this experience:

1. Chemistry is important but also technology and practical problems
2. We will design the plant in a new version (experience in pilot scale)
3. We need a further optimization in the chemistry ... and economy
4. Physical pretreatment can strongly reduce costs
5. With the participation of an engineering company we are ready to realize a new pilot plant “turn-key” (spin-off company - Resoutech)
References

For more information....


2. I. Birloaga, Recovery of base metals from waste CPU by hydrometallurgical processes, Metallurgia International (Bucharest, Romania), Volume 18, Issue 2, February 2013, pp. 69-73.


DEPARTMENT OF INDUSTRIAL AND INFORMATION ENGINEERING AND ECONOMICS

Laboratory: PROCESSES OF ENHANCEMENT AND INTEGRATED WASTE TREATMENT AND INDUSTRIAL WASTEWATER

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Thank you for your attention...