HydroWEEE Demo:
Innovative Hydrometallurgical Processes to recover Metals from WEEE including lamps and batteries – Demonstration

Recovery of precious and critical metals from Liquid Crystal Displays

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Outline

- Waste characterisation
- Extraction
- Recovery
- The whole process
- Future planning
Characterization of LCD fragments

Big plastic and glass fragments (10% of total amount)
No significant indium content

Ground fragments
Particle size up to 10 mm
Characterized & treated

A first qualitative analysis
XRF technique

Quantitative characterization

<table>
<thead>
<tr>
<th>Metal</th>
<th>Stock 1</th>
<th>Stock 2</th>
<th>Stock 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>53±6</td>
<td>130±60</td>
<td>110±20</td>
</tr>
<tr>
<td>Ga</td>
<td>8</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Mo</td>
<td>14±3</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Al (%)</td>
<td>3.3±0.7</td>
<td>5±2</td>
<td>n.a.</td>
</tr>
<tr>
<td>Ca (%)</td>
<td>n.a.</td>
<td>2.9±0.6</td>
<td>n.a.</td>
</tr>
<tr>
<td>Ce</td>
<td>n.a.</td>
<td>n.a.</td>
<td>18±1</td>
</tr>
<tr>
<td>Fe</td>
<td>3100±600</td>
<td>600±400</td>
<td>n.a.</td>
</tr>
<tr>
<td>Mn</td>
<td>53±7</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Sn</td>
<td>260±30</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

Indium in mineral ores (1-100 mg/kg)
WHY INDIUM?
Critical Raw Material for EU (2014)

Potential metals from LCD

Indium recovery:
THE WHOLE PROCESS
LEACHING PROCESS:
Experimental plan

<table>
<thead>
<tr>
<th>FACTORS</th>
<th>LEVELS</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄ conc (M)</td>
<td>1 2</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25 80</td>
</tr>
<tr>
<td>Nº leaching steps</td>
<td>1 6</td>
</tr>
<tr>
<td>Leaching time (min)</td>
<td>10 20 30 60 180</td>
</tr>
</tbody>
</table>

(solid conc 20%)

LEACHING PROCESS:
Effect of ACID CONCENTRATION

~100% extraction efficiency in both the conditions

1M
REAGENT SAVING

2M
should be used in the perspective of a multistage CROSS-LEACHING
LEACHING PROCESS:
Effect of TEMPERATURE & TIME

- **TIME**: Increase in Fe, Al, Ca concentration.
- **NO INDIUM VARIATION**: Concentrate formation.
- **10 min** is the best condition.

80°C, H₂SO₄ 2M, 60 min
- 100% indium extraction efficiency
- Low selectivity

LEACHING PROCESS:
The cross-current configuration

**TARGET**: Concentrate indium

80°C, H₂SO₄ 2M, 10 min
- Extraction efficiency DECREASE
- Indium concentration INCREASE
- Volume to purification section DECREASE
- Reagents consumption DECREASE
LEACHING PROCESS:

Economic income

The cost of reagents decreases with the number of leaching steps.

CONDITIONS FOR 1 kg end-of-life LCD panels
- Volume of plant: 5m³
- Solid conc: 20%
- Cost of H₂SO₄: 0.3 $/kg
- Cost of NaOH: 0.5 $/kg
- Indium recovery process: precipitation by NaOH

(Data based on the quotations of the last 3 years)

LEACHING PROCESS:

Environmental benefit

CO₂ emissions are remarkably reduced when the number of leaching steps increases.

10 steps allows to avoid about 90 kg CO₂-Eq.
CEMENTATION PROCESS:
Experimental plan

| FACTORS & LEVELS |
|------------------|------------------|
| FACTORS          | LEVELS           |
| Zn conc (g/L)    | 2    5   15  20  100 |
| pH               | 1   1.5  2.5  3  3.5  4 |
| Cementation time (min) | 5  10  20  30  40  50  60  240 |

CEMENTATION PROCESS:
Effect of time

- **10 min**
  - Indium recovery → 90%
  - With low amount of co-extracted metals

- **20 min**
  - Indium recovery → 99%
  - With the increase of aluminum recovery efficiency

About 60% of indium purity is the highest result obtained (on free-base zinc)
CEMENTATION PROCESS:
*Effect of pH vs Zn concentration*

- **Low conc** (2-5 g/L)
- **Medium conc** (15-20 g/L)
- **High conc** (100 g/L)

- **Zn powder**
- **pH 3**
- **pH 2**

100% Indium recovery efficiency

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**CEMENTATION PROCESS:** Proposal to solve purity issue

**ZINC AND ALUMINUM BARS**

- **INCREASE** the product purity
- **DECREASE** the loss of unreacted reagent

- **~60% eff.**
- **~90% eff.**

- **NaOH pH3**
- **6h**
CEMENTATION PROCESS: Proposal to solve purity issue

CROSS-CEMENTATION

INCREASE the product purity
DECREASE the loss of unreacted reagent

100% eff.

1st STEP

2nd STEP
**Indium recovery process:**

**MATERIAL BALANCE**

- **WASTEWATER**
- **ACID LEACHING**
- **CEMENTATION**

<table>
<thead>
<tr>
<th>Process</th>
<th>Water (m³)</th>
<th>H₂SO₄ 98% 800 kg</th>
<th>NaOH 100% 1800 kg</th>
<th>Zn 1200 kg</th>
<th>Indium 260 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washing</td>
<td>12 m³</td>
<td></td>
<td></td>
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<tr>
<td>Acid</td>
<td>3.6 m³</td>
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<td></td>
</tr>
<tr>
<td>Cementation</td>
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**WHAT ARE WE GOING TO DO?**

- Classification and recovery of all valuable fractions
- Recycle of wastewater flows within the process
- Test new high efficiency approaches to recover high purity indium from LCD scraps
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