Deliverable 3.2
Report on lamps, CRTs and LCDs, printed circuit boards, industrial and automotive catalysts

Grant Agreement number: 308549
Project acronym: HydroWEEE Demo
Project title: Innovative Hydrometallurgical Processes to recover Metals from WEEE including lamps and batteries - Demonstration
Funding Scheme: Collaborative project

Delivery date: 31th March 2017
Deliverable number: 3.2.
Workpackage number: WP3
Lead participant: University of L’Aquila
Nature: Research
Dissemination level: Restricted to a group specified by the consortium (including the Commission Services)

Author(s): Francesco Vegliò

Project Co-ordinator: Dr. Bernd Kopacek,
Kopacek KG
Tel: +43-1-2982020
Fax: +43-1-87606619
E-mail: bernd.kopacek@isl-group.at
Project website: http://www.resoutech.com/
## Contents

1. Introduction .................................................................................................................. 3
2. Spent lamps .................................................................................................................. 3
3. CRT ................................................................................................................................. 4
4. LCD process .................................................................................................................. 6
5. Lithium ion batteries process ...................................................................................... 7
6. Printed circuit boards process ....................................................................................... 9
7. Spent catalyst process .................................................................................................. 11
8. Environmental impact assessment .............................................................................. 12
9. Conclusions ................................................................................................................ 13
10. Publication list ........................................................................................................... 13
1 Introduction
Various hydrometallurgical technologies have been developed for the recovery of base, precious and rare earth elements, from 6 kind of waste materials (residues of the recycling processes of spent lamps, CRT, LCD, lithium ion batteries, waste printed circuit boards and spent catalysts). This project, which represents a continuation of the HydroWEEE project, had as main core to achieve high recovery degrees of the above mentioned elements, with high levels of purity and also to minimize the quantity of effluents. Within WP3, various research activities have been undertaken for the continuous process optimization. This deliverable describes all the developed extraction processes.

2 Spent lamps
The main cores of exhaust fluorescent lamps processing was to achieve high recovery yields for critical metals, the rare earths, with high purity of the final product using easily handling operation. Therefore the process developed within the HydroWEEE Project was successfully implemented and it has adapted to recover all rare earths contained in the phosphors of the fluorescent powders. In Figure 2.1, the main steps of the developed procedure are shown and also the brief description of the operating conditions is bellow described.

Rare earths recovery

(1) the fluorescent powder coming from the dismantling system of Relight Srl (SME partner of the project) is thermally treatment at high temperature (900°C) in presence of a air flow for 1 h in order to transform the rare earth phosphates in oxide that more easily leachable;

(2) the calcined powder is used for leaching process with sulfuric acid at a solid concentration of 10% under continuous stirring of 200 rpm for 2 h at 50°C for rare earths dissolution. The filtration step is applied for solid separation by leach liquors and then a washing with a certain volume of water is performed;

(3) the leach liquor is subjected to precipitation with oxalic acid for 1 h under continuous stirring of 200 rpm at room temperature in order to precipitate rare earth oxalates. This product is recovered by filtration and after washed with a washing with a certain volume of water. The washed solid is calcined at high temperature (600°C) for 1 h in order to obtain the final product, the rare earth oxides;

(4) the residual solution, after precipitation and filtration, is sent to wastewater treatment. This step consists of a neutralization with lime (Ca(OH)₂) for impurities removal. Then the suspension is filtered, the solid is disposed and the residual water is used as fresh water for a new cycle of leaching. The treatment with lime is performed for 1 h under continuous stirring of 200 rpm and at room temperature.

The purity of the final product achieved in according to the process described in the Figure 1 is 98.62%. The rare earths concentration in this product is 82.22% Y₂O₃, 8.38% Eu₂O₃, 2.43% Ce₂O₃, 2.29% Gd₂O₃, 1.77% La₂O₃ and 1.52% Tb₂O₃.
3 CRT
The main cores of exhaust cathode ray tubes (CRTs) processing were to achieve high recovery yields for base metals and critical metals, the rare earths, with high purity of the final products using easily handling operation. Therefore the process developed within the HydroWEEE Project was successfully implemented and it has adapted to recover yttrium and europium contained in the phosphors of the fluorescent powders and to recover zinc. In Figure 2, the main steps of the developed procedure are shown and also the brief description of the operating conditions is bellow described.

Rare earths recovery

Figure 1 Block diagram of the process waste lamps recycling
(1) the fluorescent powder coming from the dismantling system of Relight Srl (SME partner of the project) is used for leaching process with sulfuric acid at a solid concentration of 15% under continuous stirring of 200 rpm for 3 h at 80°C for rare earths dissolution. The filtration step is applied for solid separation by leach liquors and then a washing with a certain volume of water is performed;

(2) the leach liquor is subjected to precipitation with oxalic acid for 1 h under continuous stirring of 200 rpm at room temperature in order to precipitate rare earth oxalates. This product is recovered by filtration and after washed with a washing with a certain volume of water. The washed solid is calcined at high temperature (600°C) for 1 h in order to obtain the final product, the rare earth oxides.

**Zinc recovery**

(1) the residual cake coming from the leaching of rare earths, is used for a further dissolution process with sulfuric acid and hydrogen peroxide at a solid concentration of 15% under continuous stirring of 200 rpm for 1 h at room temperature for zinc dissolution. The filtration step is applied for solid separation by leach liquors and then a washing with a certain volume of water is performed;

(2) the leach liquor is subjected to precipitation with oxalic acid for 1 h under continuous stirring of 200 rpm at room temperature in order to precipitate zinc oxalate. This product is recovered by filtration and after washed with a washing with a certain volume of water. The washed solid is calcined at high temperature (600°C) for 1 h in order to obtain the final product, zinc oxide;

(3) the residual solutions, after precipitation and filtration of rare earths and zinc, are sent to wastewater treatment. This step consists of a neutralization with lime (Ca(OH)$_2$) for impurities removal. Then the suspension is filtered, the solid is disposed and the residual water is used as fresh water for a new cycle of leaching. The treatment with lime is performed for 1 h under continuous stirring of 200 rpm and at room temperature.

The purities of the final products achieved in according to the process described in the Figure 2 are 96% for rare earths product (91%Y$_2$O$_3$, 5% Eu$_2$O$_3$) and 95% for zinc oxide.
Figure 2 Block diagram of the process waste CRTs recycling

4 LCD process

The LCD process is targeted to indium recovery from the panel, residue of the manual dismantling of end of life liquid crystal displays. The research activities under WP3 have allowed to identify a promising processing route for indium recovery through the HydroWEEE technology. The target residue, i.e. the feed of the HydroWEEE plant, is a scrap coming from LCD panel shredding and grinding $< 3$mm, with a pre-sieving at 1.5 mm. The block diagram of the process is reported in Figure 3.
1) The first step includes a washing with water, in order to remove the organics from the LCD scraps. Operating conditions are: 20% solid, room temperature, 30 minutes.

2) The second step is a leaching stage with sulfuric acid 2 M, 80°C 10 minutes, carried out in a cross-current mode, in order to improve indium concentration in solution and to save the raw materials request.

3) The third step is a cementation stage with zinc, 55°C, 20 min after pH adjustment at 3 with sodium hydroxide. The achieved product is a metal concentrate, containing indium around 1%.

5 Lithium ion batteries process
LIB process here developed use black powder (electrodic active materials) previously recovered from batteries by dedicated mechanical treatments. Process included leaching, purification by precipitation, Co recovery as carbonate, and wastewater pretreatment for water recycling (Figure 4) according to the specific equipment contained in the mobile plant.
In the following each step of the process is described briefly

Leaching:

Black mass is leached using 1:10 solid to liquid ratio with H$_2$SO$_4$ 1.2 M and H$_2$O$_2$ 2.5 M under magnetic stirring at 85°C for 3h. Solid/liquid separation was performed giving: the leach liquor which was fed to the following step of purification, and a residual solid, which after mild physical and chemical treatment is recyclable graphite (0.34 Kg/Kg of black mass) containing only traces of S and O (96.5% purity as C).

Purification:

Leach liquor solution was treated by NaOH until pH 3.8 at equilibrium (0.5h stirring at room temperature). NaOH pellet was added with a dosage of 0.37 Kg/Kg of black mass. Solid/liquid separation was performed giving: the purified leach liquor to be fed to Co recovery, and Fe-bearing sludge (0.07 Kg/Kg).

Co recovery:

Purified leach liquor was added with Na$_2$CO$_3$ (0.61 Kg/Kg black mass) under stirring (0.5h) at room temperature. After precipitation CoCO$_3$ was separated by centrifugation and washed with water at pH 6 for sulfate removal (2.66 L/Kg black powder). CoCO$_3$ was dried giving a final yield of 0.98 Kg/Kg of black mass (46% purity as CoCO$_3$).

Wastewaters:

Waters emerging from Co recovery contained mainly Li, Na, sulfate and carbonate ions plus minor metal impurities (Mn, Co, Ni). Wastewater treatment included pH increase up to pH 11 by Ca(OH)$_2$ addition (0.33 Kg/Kg) in order to remove residual metals as sludge (0.07Kg/Kg of black mass). Then 60% of these treated wastewaters can be reused in leaching operations, along with washing waters of CoCO$_3$ (which are the only clean water added in each cycle 2.66 L/Kg black powder). 40% of treated wastewaters (4.5 L/Kg black mass) have to be further treated for sulfate removal by crystallization (equipment not present in the mobile unit). Adding this operation the process could result in zero water consumption reusing the condensed water for Co product washing, and Na$_2$SO$_4$ could be obtained as byproduct (96% purity as Na$_2$SO$_4$).
Characterization by acid digestion and EDX for the black mass, (CoCO3), by-products (graphite and Na2SO4), and wastes (sludge including Fe sludge from purification and metal sludge from wastewater treatment) from LIB process were reported in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Li</th>
<th>Cu</th>
<th>Ni</th>
<th>Mn</th>
<th>Fe</th>
<th>Al</th>
<th>Na</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black Mass</td>
<td>227 ± 5</td>
<td>37 ± 3</td>
<td>13 ± 1</td>
<td>55 ± 2</td>
<td>58 ± 3</td>
<td>20 ± 1</td>
<td>10 ± 2</td>
<td>&lt; LOD</td>
<td>50</td>
</tr>
<tr>
<td>Graphite</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>n.f.</td>
</tr>
<tr>
<td>Sludge</td>
<td>50 ± 2</td>
<td>14 ± 1</td>
<td>25 ± 1</td>
<td>33 ± 4</td>
<td>71 ± 6</td>
<td>100 ± 2</td>
<td>29 ± 4</td>
<td>100 ± 20</td>
<td>n.f.</td>
</tr>
<tr>
<td>CoCO3</td>
<td>220 ± 20</td>
<td>0.9 ± 0.1</td>
<td>13 ± 2</td>
<td>69 ± 3</td>
<td>74 ± 3</td>
<td>&lt; LOD</td>
<td>12 ± 1</td>
<td>5 ± 1</td>
<td>n.f.</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>&lt; LOD</td>
<td>6.6 ± 0.1</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>305 ± 6</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 1 Characterization of black mass, product (CoCO3), byproducts (graphite and Na2SO4), and wastes (sludge including Fe sludge from purification and metal sludge from wastewater treatment) from LIB process. <LOD: lower than Limit of Detection of Atomic Absorption Spectrophotometer; n.f.: not found in EDX analysis.

6 Printed circuit boards process

The main cores of waste printed circuit board processing were to achieve high recovery yields for bot. Therefore, considering the procedure developed within the HydroWEEE Project, the replacing of the electrowinning process has been successfully replaced by cementation process for Cu recovery. In Figure 5, the main steps of the developed procedure are shown and also the brief description of the operating conditions are bellow described. It is worth to mention that all the procedure steps are performed at standard temperature and pressure.

Base metals recovery

(1) the already mechanical processed material is used for the two-step counter-current leaching with sulfuric acid and hydrogen peroxide at a solid concentration of 15%, under continuous stirring of 200 rpm for 1.1/2 h each step for base metals dissolution; the filtration under pressure is applied for solid separation by liquid and then a washing with a certain volume of water is performed; this wash water is then reintegrated into the process as fresh water for a new solution preparation;

(2) the leach liquor is subjected to precipitation with polyamine solution for 30 minutes at a stirring rate of 200 rpm to recover tin, and the solid residue is washed and used further for recovery of Au and Ag; the same procedure of filtration is used for solid precipitate recovery from solution; this precipitate is also washed to remove its content of residual solution and then the water is mixed with the solution;

(3) the achieved mixture is then involved into the cementation process with metal zinc powder to recover copper; the cement is separate from solution by filtration and then this solid is washed with fresh water; the residual solution cement wash water are mixed and the stored in a tank; this can be further subjected to crystallization process to recover zinc sulphate.

Precious metals recovery

(1) the leaching with thiourea and ferric sulphate in diluted sulfuric acid media is applied on the counter current leaching residue at a solid concentration of 10% and stirring rate of 200 rpm for
1.1/2 h to extract into solution both gold and silver; filtration and washing procedure are then performed; the solution is then reused for the leaching of another solid residue coming from counter current leaching procedure using the same experimental conditions for agitation and solid concentration but with a solution make-up with a smaller content of thiourea than in previous step; after filtration the washing with same water used into the previous step is performed; the reach solution is sent to the recovery of gold and silver into their solid form and the solid residues are sent to disposal;

(2) the leaching solution is involved into the neutralization process with sodium hydroxide till pH 2 which is afterwards followed by cementation with zinc powder; the filtration procedure is then carried out and the resulted precipitate is washed with fresh water; a certain volume of the residual solution and the wash waters are mixed and used for preparation of a new solution for leaching of another solid and the rest of the residual solution is sent to the waste water treatment process;

(3) this waste water treatment consist into two steps: (i) use of hydrogen peroxide and iron sulphate (Fenton process) for the elimination of the dangerous organic compounds resulted by thiourea degradation and (ii) neutralization with lime (Ca(OH)₂) for impurities removal; after filtration, the solid is disposed of and resulted water is used as fresh water for a new solution preparation into the counter-current leaching process. The Fenton process is performed for 1 h and the treatment with lime last 2 h. Both are carried out under agitation at a rate of 200rpm.

The data of purity degrees for the products achieved are shown in Table 2.
<table>
<thead>
<tr>
<th>Product</th>
<th>Purity level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu precipitate</td>
<td>93.46%</td>
</tr>
<tr>
<td>Au and Ag precipitate</td>
<td>17.33%</td>
</tr>
<tr>
<td>Sn precipitate</td>
<td>32%</td>
</tr>
</tbody>
</table>

Table 2 Waste printed circuit boards products and their purity level

Moreover, by crystallization procedure of the zinc sulphate solution, method which is not included into the process block diagram, another product consisted of ZnSO4 may be also achieved.

What is important to remark is the fact that this procedure do not produce any waste water that must be sent to discharge, as this is fully reintegrated within the process.

7 Spent catalyst process
The main cores of spent catalysts were to achieve high recovery yield for critical metals, mainly cerium and lanthanum with high purity of the final product. Two types of catalysts were considered: fluid catalytic cracking (FCC) and automotive catalysts. In Figure 6, the main steps of the developed procedure are shown and also the brief description of the operating conditions is bellow described.

Rare earths recovery

(1) the powder of FCC catalysts is used for is used for leaching process with sulfuric acid at a solid concentration of 15% under continuous stirring of 200 rpm for 3 h at 80°C for rare earths (La and Ce) dissolution. After leaching the filtration is applied for solid separation by liquid and then a washing with a certain amount of water is performed. The solid recovered after leaching can be used in the cement industry;

(2) the leach liquor is subjected to precipitation step adding sodium hydroxide for 1 h under continuous stirring of 200 rpm at room temperature in order to precipitate rare earth double sulfates. This solid is filtered and washed to remove its content of residual solution;

(3) the residual leach liquor is sent to a wastewater treatment with lime for impurities removal. Then the suspension is filtered, the solid is disposed and the residual water is used as fresh water for a new cycle of leaching. The treatment with lime is performed for 1 h under continuous stirring of 200 rpm and at room temperature.

The purity of the precipitates was around 75–80% and the main impurities were Al (11.79% w/w) and S (10.02% w/w).

An alternative to this process is proposed. The treatment is more complex and includes: leaching with nitric acid or hydrochloric acid, filtration and solvent extraction operation. This last is performed under stirring by using 20%v/v (2-ethylhexyl) phosphoric acid (D2EHPA) in n-heptane or kerosene. Extraction of Ce and La could be done in one or two consecutive steps; the two metals are thus stripped from the organic phase by acid solution. Stripping is carried out in a single stage. Cerium and lanthanum are stripped off into the aqueous acid solution from which they precipitate with a concentrated solution of oxalic acid in the pH range of 0.5–3, adjusted with concentrated
sodium hydroxide solution. The precipitate obtained in this manner, after washing and drying, is a mixed Ce–La oxalate. Such oxalate can further be processed by calcinations obtaining mixed rare earths oxides CeO$_2$/La$_2$O$_3$. In this case aluminum concentration in the final product is reduced until 1%.

For automotive catalysts before sulfuric acid leaching it is necessary to remove the steel casing and after grinding the material to obtain a fine fraction. The powder is treated with sulfuric acid at high temperature for 3 hours and after filtration a concentrate of cerium and other metals as aluminum and iron is obtained by precipitation. The residual cake after leaching contains precious metals (as platinum) that can be recovered by leaching with strong acid conditions in presence of hydrochloric acid and hydrogen peroxide or sodium hypochlorite.

![Figure 6 Block diagram of the process FCC catalysts recycling](image)

8 Environmental impact assessment

The recycling treatments allow to achieve both the decrease of waste to dispose in landfilling sites and the production of secondary raw materials. This paragraph has the aim to report the most relevant results dealing with the environmental impact assessment of the developed processes, carried out through a life cycle analysis (LCA) approach. Figure 7 shows that the HydroWEEE-
Demo process allowed a CO$_2$ emission saving for kg of recovered metals of about 70% for CRTs and lamps, 30% for PCBs and 20% for LIBs, compared to metals primary production. In addition, the avoided waste transportation increased the emission saving up to 42% for PCBs and 30% for LIBs (Figure 7 a, d).

Figure 7 Comparison of the CO$_2$ emissions of the primary process of metals production, secondary process developed in this study from a) CRTs and b) lamps and secondary process net of transportation for the recovery of metals from c) PCBs and d) LIBs. (Functional unit: 1 ton of WEEE from traditional recycling)

9 Conclusions
Within this deliverable the main data regarding the final achieved flowsheet for the treatment of all 6 waste streams with the final products purities degree are shown. Moreover, based on the material balance of the procedures, the LCA analysis has been performed and this way the technical-economic feasibility data of each process has been demonstrated.

10 Publication list
1. I. Birloaga, I. DeMichelis, F. Ferella, M. Buzatu, F. Vegliò, Study on the influence of various factors in the hydrometallurgical processing of waste printed circuit boards for


4. I., Birloaga, F., Vegliò, Processing of waste printed circuit boards by hydrometallurgical methods for extraction of copper, gold and silver, 1st International Congress “INDUSTRIAL-ACADEMIC NETWORKS IN CooperATION ACTIVITIES FOR PHARMACEUTICAL, CHEMICAL AND FOOD FIELDS”, L’Aquila (Italy), September 17-18 2014.


6. I., De Michelis, V., Innocenzi, I., Birloaga, F., Vegliò, Progettazione, realizzazione e start-up di un impianto mobile per il trattamento di rassic , 18th International Trade Show For Material And Energy Recovery And Sustainable Development, ECOMONDO, November 5-8 2014 Rimini, Italy.


14. Francesca Pagnanelli, Emanuela Moscardini, Pietro Altimari, Thomas Abo Atia, Luigi Toro (online 2016a). Leaching of electroded powders from lithium ion batteries: optimization of operating conditions and effect of physical pretreatment for waste fraction retrieval (Waste Management) http://dx.doi.org/10.1016/j.wasman.2016.11.037


