



D6.2: Report on biohydrometallurgical materials recovery

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EXECUTIVE SUMMARY

The TREASURE project aims to create opportunities to make the automotive sector more circular. This goal is pursued through the development of tools that support the establishment of a circular supply chain, allowing for the testing of various technologies. Within the project's scope, Task 6.2 focused on enhancing hydrometallurgical recycling to recover strategic metals from end-of-life products generated by the automotive sector.

The hydrometallurgical pilot plant built under the previous EU project Fenix (grant agreement no 760792) has been reconfigured (D5.4 ANNEX 1) to be more flexible and better suited for processing various materials from the automotive sector. These materials include printed circuit boards, indium-tin oxide glass of LCDs, and in-mold electronics.

The various hydrometallurgical processes developed for recovering metals such as gold, silver, palladium, copper, tin, and indium have undergone pilot-scale testing. Successfully validating these processes at this scale has made the recycling technology suitable for marketing at the industrial level. The results significantly influence the decisions of end users, enabling them to enhance circularity in the automotive sector. This activity has been pivotal in validating the equipment's suitability and the economic feasibility of processes tested at the pilot scale for industrial application. The pilot-scale testing confirmed the effectiveness of these processes, including a significant focus on methods that allowed the reduction of freshwater usage and the introduction of wastewater treatment sections according to the Minimum Liquid Discharge (MLD) approach.

The main findings were the efficient recycling of PCBs by identifying and removing electronic components inhibiting the dissolution of metals. As a result, two hydrometallurgical processes have been developed for boards with remaining electronic components, which aim to maximize extraction yields and the purity of precious and base metals in the products. A process with low chemical consumption has been developed to treat ITO glass from LCDs. Pilot tests have confirmed the selective recovery of 98.7% of indium, resulting in a high-grade product with 99.3% purity of indium. Other key outcomes were successfully recycling silver from in-mold electronics, achieving an 82.9% recovery rate, and obtaining a 98.6% purity of the extracted silver. Additionally, it was observed that the hydrometallurgical process does not damage plastics (activity performed by TNO), leaving the possibility of recycling polycarbonate after silver recovery unchanged. Preliminary investigations have been conducted to test the reusing of recovered silver as a precursor for silver ink production in in-mold electronics, enabling the closing of the material loop.

The validated processes demonstrated innovation in reagent regeneration and water reuse, significantly reducing consumption and costs. For this reason, some of the developed and validated technologies have been included in a patent proposal submitted by UNIVAQ.

UNIVAQ organized a training session for ILSSA, which is an automotive disposer, to inform potential end-users of metal recovery technologies through hydrometallurgical processes. The training aimed at testing the processes in the hydrometallurgical pilot plant to highlight the benefits that these technologies can offer in the automotive sector.





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ANNEX 1 - Hydrometallurgical Pilot Plant Operating and Maintenance Handbook

ANNEX 2 - Materials recycling recovery assessment report





1. Introduction

1.1 Scope of the deliverable

The main objective of Deliverable 6.2 is to validate laboratory-scale hydrometallurgical processes (D5.3 and D5.4) by conducting tests on the reconfigured hydrometallurgical pilot plant. These pilot plant tests have been focused on treating various types of end-of-life materials from the automotive sector, primarily supplied by the project's industrial partners. The scaling up of these processes is a critical step in the development of these technologies. Successful testing in the pilot plant will enable the potential implementation of these processes on an industrial scale. The outcomes will influence end-user decisions regarding the adoption of hydrometallurgical processes, thus driving the automotive sector towards a circular economy.

The present deliverable was built starting from the D5.4 and includes further optimizations of the developed processes to increase metal extraction yields and improve overall efficiency. Additional optimizations were implemented to enhance the sustainability of the processes from the water use perspective, such as introducing wastewater treatment sections and reusing certain reagents. This approach aims at reducing reagent consumption and associated costs, minimizing freshwater usage (one of the major limitations of hydrometallurgical processes), and decreasing wastewater generation using an MLD approach, compared to other existing hydrometallurgical processes [1] and others developed by UNIVAQ that have been realized at industrial level. Some of the developed processes can also be considered bio-hydrometallurgical because certain reagents used, such as acetic acid for treating printed circuit boards, can be biologically produced through acetogenesis using inorganic substrates like CO₂ and CO with acetogenic bacteria, as well as through aerobic fermentation. Additionally, it is environmentally friendly to use L-ascorbic acid (vitamin C) to precipitate and recover gold from the solution in which it was dissolved. Ascorbic acid can also be produced through fermentation with microorganisms. Therefore, hydrometallurgical processes utilize reagents that can be produced biologically and can thus be defined as bio-hydrometallurgical processes.

Specifically, the hydrometallurgical processes for the treatment of printed circuit boards, inmold electronics, and indium-tin oxide glass of LCDs have been validated at the pilot scale. Regarding the PCBs, among those of the different critical car parts, those of combimeters have been selected based on the thermodynamic rarity ranking conducted by UNIZAR. Various types of in-mold electronics have been processed, as they are an emerging technology that could soon partially replace conventional printed circuit boards, even in the automotive sector. Additionally, ITO glass, commonly used in LCDs, is widely utilized in the automotive sector for infotainment systems and other applications.

In each hydrometallurgical process, pilot scale tests were described, and the main results have been discussed. Next, a process analysis was carried out by defining material and energy balances, followed by a preliminary economic analysis to assess the process's economic feasibility. This was followed by a preliminary discussion to understand the investment margins required for implementing the different processes in an industrial plant. Additionally, the market trends and forecasts for various materials, as well as the demand for supply of different recovered metals including gold, silver, copper, tin, palladium, and indium, were evaluated. Considerations were also given to the demand for mineral resources in the EU economy, particularly in the market for electric vehicles as part of low-carbon energy solutions.

Furthermore, the deliverable will detail the training session for the use of the hydrometallurgical pilot plant, conducted by UNIVAQ personnel for ILSSA as an industrial partner and





representative of end-users interested in hydrometallurgical recycling technologies. The operating and maintenance handbook of the hydrometallurgical pilot plant is provided as an annex to this deliverable. ILSSA has highlighted the advantages of using hydrometallurgical processes for recycling automotive materials. They compared the current situation of automotive dismantlers with the benefits of using hydrometallurgical technologies validated in the EU Treasure project.

1.2 Contribution to other WPs

The main links of this deliverable with other tasks are related to the line of Treasure pilot plants. In fact, to increase recycling efficiency, some specific SMDs have been identified to be disassembled from PCBs before hydrometallurgical treatments. This information was transferred to POLIMI, which, in Task 6.1, tested the disassembly of these SMDs thanks to the advances they obtained with COBOT technology. In addition, together with TNO, the circularity of silver in in-mold electronics has been studied thanks to the support of GENESINK (advisory board member) as the end-user of silver for its use as a precursor to producing silver ink. In addition, the in-mold electronics output of the hydrometallurgical process, that is, the solid residue of the process, was used by TNO for investigations on the recycling of polycarbonate.



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2. Hydrometallurgical pilot plant tests

The hydrometallurgical processes developed at the laboratory scale, as outlined in D5.4, have undergone testing in the reconfigured hydrometallurgical pilot plant to evaluate their efficacy at a larger scale. This step represents a significant milestone in the development of these technologies, as successful testing in the pilot plant will allow for the potential implementation of these processes at an industrial scale. The outcomes of this testing will be critical in informing the decision-making process regarding the future of these technologies.

The pilot scale hydrometallurgical processes that have been investigated include the following:

- 1) Recycling of IMEs for the recovery of silver (2.1).
- 2) Recycling PCBs from car dashboards to recover base and precious metals (2.2).
- 3) Recycling of ITO glass from LCDs for the recovery of indium (2.3).

2.1 Recycling of in-mold electronics

The following paragraph presents the findings of the pilot plant tests conducted on the IMEs. The primary objective of these tests was to identify any potential issues during the scale-up process and to develop a more sustainable process, mainly from a water use perspective, than the one outlined in D5.4 (ANNEX2). Specifically, the aim was to reduce water consumption by including a wastewater treatment section that allows water reuse. This experimentation proved to be successful in addressing issues related to the leaching and electrodeposition stages. As a result, we validated an optimized process for the recovery of silver from IMEs on a pilot scale using an MLD approach.

2.1.1 Pilot tests

The pilot tests utilized various types of IMEs, including thermoformed, full silver area, elongated, and roll samples, which were provided by TNO. All samples had a flexible polycarbonate substrate and a silver ink layer of varying shapes and amounts. Some samples also contained small SMDs such as LEDs. The mixture of IMEs contained 0.97% \pm 0.37% of silver content. The number of components used from each sample varied depending on the specific test. To accurately calculate the recovery rate, the amount of silver that was not recovered in the solid residue was experimentally determined. The recovery rate was then calculated using the following formula:

dissolved metal, % =
$$\frac{Ag_L}{Ag_L + Ag_S} \times 100$$
 (1)

where Ag $_{L}$ is the amount of silver dissolved in the leach liquor and Ag $_{s}$ is the amount of silver in the solid residue, i.e. not dissolved.

The following are details of the experimental operations conducted on a pilot scale, and the primary outcomes of preliminary tests. This test revealed some issues, subsequently reported, that were corrected in the next tests. The process has been tested according to the operative conditions reported in Table 1.





Preliminary pilot plant test: operative conditions						
leaching (1 st step)	leaching (2 nd step)				
solid (IMEs)	4 kg	make-up of chemicals				
solution	60 litres	CH ₄ N ₂ S	0.70 kg			
H ₂ O	58.3 kg	Fe ₂ (SO4) ₃	1.80 kg			
CH ₄ N ₂ S	1.20 kg	H ₂ O	20.0 kg			
Fe ₂ (SO4) ₃	1.35 kg					
H ₂ SO ₄ (50%)	2.37 kg					
note: time of reaction 1 h, room temperature, no stirring		note: the 2 nd step has been conducted with the same solid and solution, time of reaction 1 h, room temperature, no stirring				
electrodeposition						
voltage: 1.3 V 1 cathode: co						
electrodes distance: 3	cm	2 anodes: titanium oxides	n covered by a mixture of			

Table 1. Operative conditions of the preliminary pilot plant test

The equipment used for the test is described briefly below. The chemical reactor for leaching operations has been selected based on the type of material. The selected reactor (R103) has a capacity of 100 litres and is built in polypropylene. It is equipped with a septum that has lots of 1.2 mm openings allowing the solution to pass through but not the IMEs. This method eliminates the need to discharge solids from the reactor before the second step of leaching and reduces water consumption by skipping the washing process. Since this reactor lacks a specific stirrer for mixing, the leaching solution was prepared in another reactor equipped with a stirrer to ensure vigorous mixing. To separate solid particles from the leach liquor, a 10 µm porous nylon cartridge filter was used for the filtration. After completing two stages of leaching, the solution rich in silver is sent to the precious metals electrolytic cell (CE102) for the recovery of silver powder. To appraise the efficacy of the process multiple samples were taken at various stages of the process from both solutions and solids. The samples were subjected to rigorous evaluation to determine the efficiency of the process. The evaluation results were used to assess the overall effectiveness of the process in terms of its ability to recover silver in a pure form and control the consumption of reagents according to what was observed at the scale.

The test consisted of the following operations:

- 1. Load IME samples into the chemical reactor R103.
- 2. Prepare the leaching system in the chemical reactor R102.
- 3. Load the solution in contact with the solid into the chemical reactor R103.
- 4. Allow for the chemical reaction to occur in R103.
- 5. Filter and discharge the leach liquor from the 1st step into R102.
- 6. Add ferric sulphate and thiourea to the solution in R102 for a make-up.
- 7. Repeat steps 3 and 4.
- 8. Filter and discharge the final leach liquor into a tank.
- 9. Load the precious metals electrolytic cell CE 102.
- 10. Set the rectifier voltage.
- 11. Begin the electrodeposition stage.
- 12. Discharge the solution into a tank and recover the cathode with the silver deposit.





2.1.1.1 Preliminary pilot tests

The purpose of the preliminary pilot tests was to examine the feasibility of recycling silver from IME while assessing the robustness of the process investigated at the laboratory scale. The tests were also aimed at identifying any potential issues that may arise during the recycling process and devising corrective actions to address them. The results of these tests will provide valuable insights into the viability of recycling silver from IME and help determine the best possible requirements for scaling up the process in a dedicated industrial plant.

In Figure 1, photographs of the samples used to test the hydrometallurgical process are shown just after loading into the R103 reactor, before starting the leaching operations.



Figure 1. Flowsheet of the hydrometallurgical process for the recycling of Ag from IMEs

Table 2 shows the results obtained from the leaching stages.

Results of the leaching stages (method: ICP-OES analysis)						
Stage Ag concentration, mg/L Ag dissolution, %						
1 st leaching (60 litres)	149.2	28.7				
2 nd leaching (80 litres)	316.7	81.2				

Regarding the leaching stage, compared to the results obtained on a laboratory scale, it can be observed that a yield significantly lower in the first leaching step, 28.7% silver extraction compared to 69.5% (D5.4 Annex 2), was achieved. So, the first issue raised in the scale-up is as follows:

- not all IMEs were well immersed in the leaching solution.

This issue is closely related to the scale of the process and depends on the shape of the equipment and the size of the material to be processed. For this reason, an additional 20 litres have been added for the second step of leaching, reducing the solid concentration to 5% wt./v. Proceeding in this manner, a cumulative silver yield of 81.2% was obtained after the two leaching steps, which was almost in line with the 85% yield obtained at the laboratory scale.

Instead of reducing the solid concentration and therefore the productivity, this problem could be solved by cutting each sheet of IMEs into four parts or by designing specific equipment with a bath-shaped configuration in a dedicated plant for the treatment of IMEs. Generally, the choice of equipment significantly affects the exposure of the solid to the reagents and thus also the metals recovery rate. In this case for the following tests, each sheet has been cut into some parts to ensure the solid was properly exposed to the solution during the leaching phase.





The use of reagents like thiourea, sulfuric acid, and ferric sulphate, determined through solution titration, has been confirmed to closely match the outcomes of laboratory-scale tests. This consistency highlights the reliability and accuracy of the process.

Figure 2 shows a picture of the leaching stage in the R103 chemical reactor and IMEs samples after leaching, where the changes in the colour of the ink layer are evident to testify that silver dissolution occurred.



Figure 2. Leaching operation in R103 (left side), and samples after leaching (right side).

The recovery of silver from the leach liquor has been performed through the electrolytic cell CE102 following the conditions in Table 1. Throughout the test, the concentration of silver and other impurities such as copper in the solution was monitored for up to 5 hours, based on the results obtained from D5.4. The results of the electrodeposition stage are reported in Table 3.

Electrodeposition							
Time h	Concentratio	n in the solution	Recovery on the cathode				
Time, fi	Ag, mg/L	Cu, mg/L	Ag, %	Cu, %			
0	316.7	126.4	0.0	0.0			
1	303.1	127.2	4.3	0.0			
2	234.3	125.6	26.0	0.6			
3	231.9	123.0	26.8	2.7			
4	178.7	123.7	43.6	2.1			
5	163.9	123.6	48.2	2.2			

Table 3. Silver and copper concentration monitoring during the electrodeposition (preliminary test).

Based on the voltage setting (1.3 V) this step aimed to selectively recover silver from the solution. The results show that after 5 hours of electrodeposition, a silver recovery of 48.2% has been achieved while the copper contamination is low, about 2%. Compared to the laboratory test has been observed a lower current density (40 A/m²) because of a lower supplied current (3.0 A). Therefore, the following outcomes have been achieved:

- Silver recovery is low because of the low current density.
- Copper remains in the solution and does not affect the selectivity of the operation.

To address the first point, it is essential to raise the current without increasing the voltage to maintain efficiency in selectively recovering silver while retaining copper in the solution. Possible





solutions to increase the current include enhancing agitation in the cell to facilitate mass transfer and reducing the distance between electrodes to minimize resistance. To increase the current and consequently the current density, the electrodes will be brought closer together during future tests, as increasing the recirculation flow of the pump is not an option with this equipment.

Next, an additional important aspect involved the retrieval of the silver powder from the cathode and its analysis to determine its purity. In Figure 3 a picture of the deposit on the copper cathode is shown.



Figure 3. Deposited silver powder on the copper cathode.

In Figure 4, an extract of XRF semi-quantitative analysis on the recovered silver powder is shown. It detects a low silver purity that stops at around 45%, a remarkable copper impurity at around 30%, and other relevant impurities such as sulphur (4.5%), potassium (2.2%), and iron (1.2%).

12	Mg	Magnesium	< 0.0020 %	41	Nb	Niobium	< 0.00010	%
13	AI	Aluminum	< 0.0020 %	42	Mo	Molybdenum	0.00107	%
14	Si	Silicon	< 0.00051 %	47	Aq	Silver	44.76	%
15	P	Phosphorus	< 0.00030 %	48	Cd	Cadmium	0.03458	%
16	S	Sulfur	(4.518 %)	50	Sn	Tin	< 0.00030	%
17	CI	Chlorine	0.07022 %	51	Sh	Antimony	< 0.00030	%
19	K	Potassium	(2.209 %)	52	To	Tellurium	< 0.00030	0/
20	Ca	Calcium	< 0.0010 %	53	I	lodine	< 0.00030	0/2
22	Ti	Titanium	0.01304 %	55	Ce	Cosium	0.0261	9/
23	V	Vanadium	< 0.00010 %	56	Ra	Barium	< 0.0201	0/
24	Cr	Chromium	0.00262 %	50	Da	Danum	< 0.00020	70
25	Mn	Manganese	0.00547 %	57	La	Lanmanum	< 0.00020	70
26	Fe	Iron	(1.176 %)	58	Ce	Cerium	< 0.00020	%
27	Co	Cobalt	< 0.00030 %	59	Pr	Praseodymium	0.00452	%
28	Ni	Nickel	< 0.00005 %	60	Nd	Neodymium	0.00384	%
29	Cu	Copper	(30.18 %)	72	Hf	Hafnium	< 0.00010	%
30	Zn	Zinc	0.07986 %	73	Ta	Tantalum	0.519	%
31	Ga	Gallium	< 0.00005 %	74	W	Tungsten	0.1171	%
32	Ge	Germanium	< 0.00005 %	80	Hg	Mercury	< 0.00010	%
33	As	Arsenic	< 0.00005 %	81	TI	Thallium	0.00294	%
34	Se	Selenium	< 0.00005 %	82	Ph	Lead	0 7030	9/0
35	Br	Bromine	0.00451 %	83	Ri	Riemuth	< 0.00010	0/
37	Rb	Rubidium	< 0.00005 %	00	Th	Therium	0.00010	0/
38	Sr	Strontium	< 0.00005 %	90	10	Inonum	0.01102	70
39	Y	Yttrium	0.00070 %	92	0	Uranium	0.00533	70
40	Zr	Zirconium	< 0.00010 %					

Figure 4. XRF semi-quantitative analysis on the powder recovered from the copper cathode.





Since the copper concentration in the solution after completion of the electrodeposition test remained almost constant compared to the initial concentration (Table 3), copper contamination is inevitably due to the manual recovery of the powder from the cathode surface. The powder recovery operation, although carried out with care, is to partially scratch the material from which the cathode is made, i.e., copper.

Therefore, to solve the criticalities highlighted by the preliminary silver electrodeposition test, the following countermeasures were taken:

- The electrodes have been brought as close as possible, up to 1 cm distance, to increase the current supplied at an equal voltage (1.3 V), as it is necessary to avoid the simultaneous recovery of copper from the solution.
- Three consecutive electrodeposition tests were carried out without removing the powder deposited at the end of each test but recovering it directly to the end to have a ticker layer and potentially reduce copper contamination.
- From the silver powder deposited on the cathode two different samples were collected, one more superficial and another more internal in contact with the cathode, so that they can be analysed separately, and the effect of copper contamination can be evaluated.

On the basis of the new operating conditions adopted, the average current increased to 5.0 A, and consequently, the current density increased to 70 A/m². In Table 4, silver and copper concentrations in the solution of the electrolytic cell have been monitored as a function of time.

Electrodeposition							
Time h	Concentratio	n in the solution	Recovery on the cathode				
Time, fi	Ag, mg/L	Cu, mg/L	Ag, %	Cu, %			
0	312.5	128.2	0.0	0.0			
1	251.8	127.8	19.4	0.3			
2	204.8	129.1	34.5	0.0			
3	165.4	125.3	47.1	2.3			
4	126.6	122.7	59.5	4.3			
5	95.1	121.9	69.6	4.9			

Table 4. Silver and copper concentration monitoring during the electrodeposition (second test).

It can be observed that, compared to the preliminary test, in this case, the increase in current allowed for an increase in recovery until 70% of the silver recovered from the solution. As for copper, the increase in current showed a slight increase in copper recovery, from 2-3% of the preliminary test to almost 5% of this test. However, it is still a very low recovery, even more so considering that the amount of copper in the solution, compared to that of silver, is less than half.

To also monitor the energy consumption, in Figure 5, the recovery of silver as a function of the current efficiency is shown. The current efficiency is calculated by considering the electric charge effectively used for silver recovery compared to that available in the bath.









Since the solution after electrodeposition is not discharged but is reused in subsequent cycles, it is not cost-effective from an energy point of view and therefore economical to recover all the dissolved metal in a single step. So, this graph allows us, at a qualitative assessment, to identify a time for which it is convenient to interrupt the electrodeposition, that is, that time beyond which we notice that the increase in recovery of the metal is lower than the decrease in current efficiency, i.e., significantly increases the energy consumption per kg of recovered metal.

As a result, 50% of the silver is recovered after around 3 hours, and the current efficiency is slightly under 4%. Silver is further recovered at higher times but at the expense of significant energy consumption. Although the current efficiency value is poor, it is comparable to electrodeposition-based precious metals recovery results [2]. Therefore 50% is the recovery of silver at 3 hours, but this does not imply that only 50% of the silver is recovered from the leach liquor after electrodeposition. The solution from which 50% of the silver was recovered is reused in the next batch as a leaching solution with a make-up of some chemicals to treat new IME samples. As a result, the unrecovered silver remains in the cycle and is returned to another electrodeposition. In Figure 6, the silver recovery and the current efficiency curves as a function of time are shown for the electrodeposition test of the second cycle.



Figure 6. Silver recovery vs current efficiency as a function of time during the electrodeposition of the second cycle.





For the second cycle of electrodeposition at three hours 65% of silver recovery has been achieved, in correspondence of 5.7% of current efficiency. The increase in silver recovery compared to the electrodeposition of the first cycle, as well as the slightly shorter time and an increase in current efficiency, are dependent on the silver concentration in this solution, which is higher than that of the first cycle (around 470 mg/L versus 315 mg/L).

Again, the residual solution is reused for a third cycle of the process, by performing leaching of new IMEs samples after a chemical make-up and then a final electrodeposition of silver, in this case by increasing the time to recover almost all the silver from the solution, regardless of the three hours assumed for the optimization of the energy consumption. Figure 7 shows silver recovery and current efficiency curves for the electrodeposition of the third cycle.



Figure 7. Silver recovery vs current efficiency as a function of time during the electrodeposition of the third cycle.

In this case, for the electrodeposition of the third cycle, since the solution after electrodeposition must be transferred to the wastewater treatment section, the silver has to be recovered as much as possible. As noticeable by the figure after 7 hours of electrodeposition around 95% of silver is recovered.

Therefore, by summarizing the electrodeposition efficiency in terms of silver recovery per each cycle, after 3 hours it was obtained a silver recovery of 50.4% in the first cycle and 65.3% in the second cycle. In the third cycle, 95.2% of silver recovery has been achieved after 7 h of electrodeposition. By considering that the amount of not recovered silver in the first and in the second cycle is not lost because it remains in the solution to be reused for the subsequent cycles, to estimate the overall silver recovery with the electrodeposition operation some calculations have been done by keeping constant the efficiency of the leaching. In Table 5 some calculations to show the effective silver recovery are reported based on the capacity of the electrolytic cell (20 liters).





Recovery of silver by electrodeposition after three cycles of the recycling process							
Cuelo	leaching		before EW	after EW			
no.	Ag dissolved, g	Ag residua	5 al*, g	Ag, g	Time, h	Ag recovery, %	Ag recovered, g
1	6.25	0.00		6.25	3.00	50.4	3.15
2	6.25	3.10		9.35	3.00	65.3	6.11
3	6.25	3.24		9.49	7.00	95.2	9.03
Overall Ag recovery after three cycles							
Dissolved Ag, g Re			ecovered Ag by EW, g		Recovery Ag, %		
18.75			18.29	97.5		7.5	

Table 5. Preliminary pilot test: silver electrodeposition per each cycle and overall recovery calculations (*Ag residual in the solution from the previous cycle).

As a result, by optimizing the electrodeposition stage and conducting pilot testing for each cycle's solution, an overall silver recovery of 97.5% in a full batch was obtained. This efficiency was achieved with an energy consumption of 8.5 kWh/kg of recovered silver.

The obtained powders by a full batch and the sludge left on the bottom of the bath after discharging the solution are shown in Figure 8. Compared to Figure 3 is evident that the layer of the powder on the copper cathode is significantly thicker.



Figure 8. Left side: deposited silver powder on the copper cathode after three cycles of electrodeposition; right side: powder in the bottom of the electrolytic cell.

For the analysis to determine the silver purity, three distinct samples were collected: the first sample consisted of the most superficial layer of the deposit, which was manually scraped off using a laboratory spatula; the second sample comprised the layer directly in contact with the copper cathode, which was detached by employing a laboratory spray; and finally, the third sample consisted of the sludge that settled at the bottom of the cell during the electrodeposition process. The purpose of separating the first two samples during the powder collection from the cathode was to prevent copper contamination during manual scraping.

XRF semi-quantitative analyses have been conducted for the three samples after drying at 105 °C, the results in terms of the main detected elements are reported in Table 6.





Powders' characterization recovered by electrodeposition								
sample no.	1 2 3							
description	the superficial layer of the deposit	the internal layer of the deposit	sludge settled in the bottom of the bath					
Ag, %	55.0	40.2	1.73					
Cu, %	11.5	35.6	0.52					
S, %	8.19	8.56	17.2					
Fe, %	1.07	0.13	0.75					

Table 6. XRF semi-quantitative analyses on the three samples of powders recovered after electrodeposition.

From the table, it is evident first that the purity of silver in the powder is low, in the range of 40– 55% as regards the powder deposited on the copper cathode. Copper is the primary contaminant, and its presence is attributable to the laborious procedure of recovering the powders from the copper cathode, as the concentration of copper in the solution remains practically constant after electrodeposition. Consequently, as can be shown by comparing the first two samples, copper contamination is dependent upon the recovery of copper particles from the cathode material. It is found that the second sample, which comes into close touch with the copper bar, is more contaminated with copper and has a lower purity of silver than the first. The third sample recovered on the bottom of the electrolysis cell, however, has a low content of silver as well as copper but is composed mainly of sulphur due to residues from the sulphate-based leach liquor. Mainly for the last sample, but also for the first two samples, since silver, copper, and iron are as metal and only sulphur is in a non-metal form like sulphates, it appears evident that a high content of organic matter is still present in the samples. For this reason, the samples were thermal treated at 550 °C for 1 hour to detect the loss on ignition (LOI) and to further refine the samples in terms of silver grade. In Table 7, XRF analysis on the thermal treated samples has been again conducted with also the correspondent LOI. The percentage of LOI is a measure of the organic matter content.

Powders' characterization after thermal treatment						
sample no.	1	3				
description	the superficial layer of the deposit	the internal layer of the deposit	sludge settled in the bottom of the bath			
LOI, %	3.2	< 0.1	65.6			
Ag, %	61.3	42.1	71.7			
Cu, %	15.6	37.6	15.5			
S, %	3.98	5.52	2.87			
Fe, %	1.11	0.28	2.62			

Table 7. XRF semi-quantitative analyses on the three samples after 550 °C thermal treatment and LOI.

The table analysis reveals first the organic fraction content, which is 3.2% for the most superficial layer and 0.1% for the inner layer of the powders deposited on the cathode. Certainly, the presence of organic material depends on the presence of leach liquor residues in contact with the powder. Indeed, no organic matrices were found in the inner layer. This result is confirmed





by the high LOI concentration of the sample collected from the bottom of the electrolysis cell. Silver purity was determined at 61.3% for sample 1 powder, 42.1% for sample 2, and 71.7% for sample 3. Sample 1 is the most relevant since it is more indicative of the operation and is less affected by the contamination of the cathode's material. Furthermore, even after thermal treatment, sulfur concentrations remain in the 3-5% range, depending on the sample type. It is crucial to note that sulfuric acid was utilized in the leaching solution. Most likely, the sulfur is complex with other components and hence cannot be eliminated at 550 °C. This information can be useful for future testing because it is necessary to properly wash the powder recovered by electrodeposition right after the operation to remove as much residual leach liquid as possible. Otherwise, the quality of the recovery powder can be affected.

To increase the silver purity of the powder recovered from the pilot plant, a refining process has been tested. It includes a treatment at 550 °C for the removal of the organic compounds and a subsequent hydrometallurgical refinement consisting of a leaching and another silver selective electrodeposition, carried out on a laboratory scale. This refining operation allowed the achievement of purity in silver in the range of 98–99%.

The main issues raised by the pilot-scale experimentation of the silver recycling process from IMEs and possible solutions to adopt are summarized in Table 8.

	Issue vs solution for the preliminary pilot test activities					
lssue no.	Main raised issue	Adopted solution	Other solutions to be adopted			
#1	Immersion of IME whole sheets during the leaching stage	To reduce the solid concentration by increasing the volume of the leaching solution or to cut the IME samples in some parts.	A specific chemical reactor can be designed in a dedicated industrial plant for the treatment of IMEs without any grinding (average sample size 35x20 cm) to maintain at least 10% wt./v as solid concentration.			
#2	Low current during the electrodeposition stage	Reducing the distance between the electrodes				
#3	Quality of the final product, copper contamination	Recover the deposited powder after more than one electrodeposition test to obtain a thicker deposit	Use a silver cathode to avoid contamination of the cathode material			

Table 8. Issues raised from initial pilot-scale experiments and potential measures to be taken.

2.1.1.2 Validation pilot test

A further pilot scale test has been carried out based on the corrective actions identified by the preliminary tests. For electrodeposition, a silver bar as a cathode was used to reduce copper contaminations in the final product. Due to the use of the majority of IME available samples for the preliminary tests, lower volumes have been used to carry out the present test.

Leaching operations have been performed at the same conditions in terms of chemicals and time but working at a lower solid concentration (5% wt./v) and cutting IME sheets in four parts





to be sure that all the samples were well immersed in the leaching solution, according to the resolution of issue #1. In Table 9 the results of the two stages of leaching of the first cycle have been reported.

Results of the leaching stages – 1 st cycle (method: ICP-OES analysis)					
Stage Ag concentration, mg/L Ag dissolution, %					
1 st leaching (40 litres)	294.1	66.1			
2 nd leaching (40 litres)	375.6	84.4			

Table 9. Results of the final pilot plant test, leaching operations.

This test confirmed the results of the laboratory scale both for the first and the second stages of leaching. An overall dissolution of silver of 84.4% has been achieved. Results of the leaching operations obtained for the first cycle have been confirmed also for the next cycles with good replicability. Certainly, for industrial plant design, it would be necessary to consider the need for a specific chemical reactor to ensure better exposure to IME without reducing size to avoid a decrease in productivity.

Therefore, the recovery of silver from the solution has been performed with the electrolytic cell by working with the minimum distance between the electrodes to solve issue #2 and by using a silver cathode to solve issue #3 related to the copper contamination in the deposited powder.



In Figure 9 the electrolytic cell equipped with the silver cathode and two anodes is shown.

Figure 8. Electrolytic cell equipped with the silver cathode for the optimized pilot test.

The hydrometallurgical process has been again tested for three cycles to practically evaluate the leaching and electrodeposition efficiencies in terms of silver recovery and energy consumption. Cycles have been conducted according to the make-up of the chemicals that were determined by the laboratory test and also used for the preliminary pilot plant test.

In Figure 9 the results of the electrodeposition tests for each cycle in terms of silver recovery and current efficiency as a function of time are shown.







Figure 9. Silver recovery vs current efficiency as a function of time during the electrodeposition of the third cycle for the optimized pilot test - a) first cycle; b) second cycle; c) third cycle.

Concerning the electrodeposition results, silver recovery was slightly higher than the preliminary test and also the silver purity in the recovered powder was significantly higher without the need for a refining treatment. In Table 10 a summary of the results obtained with the final optimized test is reported.

Results of the final pilot test for the recycling of Ag from IME					
Cuelo no	Ag recovery, %				
Cycle, no.	Leaching 1 st	Leaching 2 nd	Electrodeposition		
1	66.1	84.4	65.1		
2	64.2	83.4	73.1		
3	65.1	84.8	96.1		
Batch (1+2+3)	65.1	84.2	98.4		

Table 10. Results of the optimized pilot tests for the recycling of Ag from IME.

To summarize, the validation pilot test achieved an overall silver recovery of 82.9% after running three cycles. The average silver dissolution rate obtained was 84.2%, while the recovery of silver from the leach liquor by electrodeposition was 98.4%. It is accurate to consider the average value of the three cycles for silver recovery in the leaching stages but not in the case of the electrodeposition. This is because any unrecovered silver from the first two solutions is reused in the subsequent cycles. The total amount of silver recovered from the three cycles by





electrodeposition is calculated by comparing it to the dissolved amount. In addition, an energy consumption of 5.3 kWh/kg of recovered silver has been obtained.

In Figure 9 the silver deposit on the silver cathode from the electrolytic cell is shown as well as the recovered silver powder.



Figure 9. Silver powder recovered from the IME recycling process tested at pilot scale – a) silver deposit on the cathode; b) recovered silver powder.

The powder has been subjected to quantitative chemical analysis to determine the silver purity (ICP-OES) and to XRD analysis to identify the form of silver. In Table 11, the chemical analyses have been reported. A silver purity of 98.6% has been achieved, while the main contaminants are calcium sulfate (1.07%), iron 0.26% and copper 0.10%.

Table 11.	Silver	powder	characterization.

Silver powder quantitative chemical analyses (method: ICP-OES)			
metal/salt wt. %			
Ag	98.57		
CaSO ₄	1.07		
Fe	0.26		
Cu	0.10		

In Figure 10 the XRD spectrum of the powders in the range of 0-70 degrees to evaluate the form of the silver has been shown. Based on this analysis it is confirmed that silver in the powder is in its metallic form.







Figure 10. XRD analysis on the silver powder.

2.1.1.3 Sustainable practices for managing pilot plant wastewater

The wastewater generated by the three processing cycles conducted on a pilot scale was then characterized to determine the main metals and their organic load. Tests have, therefore, been carried out for treating this wastewater on a laboratory scale. Considering the design of a specific industrial plant for the recovery of silver from IME, it will also need to include the wastewater treatment section. This step will ensure that the wastewater generated during the recovery process undergoes effective treatment before being reused or discharged. Implementing a comprehensive wastewater treatment section will be crucial for maintaining environmental compliance in an industrial plant.

In Table 12 the composition of the wastewater generated by the pilot test has been reported.

Wastewater composition (method: ICP-OES and HACH-Lange)			
рН	1.39		
COD 14480 mg/L			
Fe 8688 mg/L			
Cu 117.4 mg/L			
Ag 18.5 mg/L			

Table 12. Hydrometallurgical wastewater composition.

The high level of COD (Chemical Oxygen Demand) and Fe in the wastewater is due to the chemicals that have been used in the hydrometallurgical process, essentially thiourea and ferric sulphate in acid media.

Wastewater treatment has been studied by adopting the Fenton process which falls among the advanced chemical oxidation processes, the treatment is then completed by a lime addition stage to align the pH in the neutral values and to transfer the pollutant into sludges. Wastewater treatment has been studied by adopting the Fenton process which falls among the advanced chemical oxidation processes. The Fenton process is considered highly successful in wastewater





treatment due to its ability to generate hydroxyl radicals for effective oxidation. During Fenton oxidation, hydroxyl radicals are produced through a chemical reaction that includes ferrous ions and hydrogen peroxide. Fenton reagents (iron and hydrogen peroxide) initiate a chain reaction that proceeds as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$$
(1)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O_2H \bullet + H^+$$
 (2)

As illustrated in the reactions ferrous iron (Fe²⁺) initiates the reaction and catalyzes the decomposition of H_2O_2 into hydroxyl radicals.

To determine the best operative conditions the Fenton process has been studied by factorial experimentation. Experiments were performed by working at constant pH (1.39), room temperature, and only the effect of two main factors (Fe (II) and H_2O_2) was investigated by using 2^2 full factorial plans with three centre points to estimate the experimental error. The effect of Fe (II) in the abatement of COD has been investigated in the range of 3-12 g/L while H_2O_2 (30%) is in the range of 5-15 as a v/v percentage. The experimental conditions and the results of the full factorial plan are given in Table 13.

Bun	A: H ₂ O ₂	В:	COD removal,	Fe removal,	Cu removal,
Kuli	(30%) % v/v	Fe (II) g/L	%	%	%
1	5	3	66.7	98.6	99.7
2	15	3	92.4	99.9	98.2
3	5	12	63.8	97.0	99.9
4	15	12	89.9	98.9	95.2
I	10	7.5	84.4	98.8	99.4
II	10	7.5	86.2	96.5	99.7
	10	7.5	83.7	96.5	99.7

 Table 13. Experimental conditions and results of 2² full factorial plan.

Analysis of variance (ANOVA) conducted using Yates' algorithms, the most used technique for the elaboration of factorial plans, revealed factor A (hydrogen peroxide) as the sole significant factor exceeding the 95% confidence level. Moreover, it's noteworthy that the wastewater already contains iron, with a concentration of 8688 mg/L, for this reason, factor B is not significant for the COD removal.

For optimization purposes, based on the comparison of experimental and critical Fisher ($F_{experimental} > F_{critical}$) star points were added to find an accurate model for the COD removal. The results obtained by the addition of star points are provided in Table 14.

Additional	A: H ₂ O ₂	В:	COD removal,	Fe removal,	Cu removal,
Run	(30%) % v/v	Fe (II) g/L	%	%	%
1	2.93	7.5	59.9	100.0	99.8
2	17.07	7.5	92.3	100.0	97.9
3	10.0	1.14	94.3	100.0	91.4
4	10.0	13.86	87.0	99.9	99.8

Table 14. Experimental conditions and results of star points.





Based on the experimental results in terms of COD removal, it can be noted that run 3 in Table 14, with less hydrogen peroxide, showed higher efficiency than run 2, suggesting excess iron and hydrogen peroxide inhibit mineralization. This imbalance leads to incomplete oxidation, reducing mineralization efficiency, as indicated in the literature [3].

ANOVA was carried out with Yates' algorithm to evaluate the effect of the two investigated factors and their interaction on the COD removal. The significance of the effects was assessed by the F-test method at a confidence level of 95%, which permitted us to evaluate if the effects were significant compared to the experimental error of the tests (Table 15).

Terms	Coefficients	Std. Error	P-value	1-р	Significance, %
intercept	84.74	-	-	-	-
X1	12.21	1.26	2.01E-04	0.9997	99.97
X ₂	-2.00	1.26	1.75E-01	0.8253	82.53
x ₁ x ₂	0.10	1.79	9.59E-01	0.0413	4.13
x ₁ ²	-5.63	1.50	1.34E-02	0.9866	98.66
x ₂ ²	1.66	1.50	3.20E-01	0.6800	68.00

Table 15. Yate's algorithm for the central composite design, confidence level 95%.

The ANOVA showed that significant factors are H_2O_2 with a positive effect and its square with a negative effect. The negative coefficient for the squared term of H_2O_2 concentration shows that initially adding more H_2O_2 improves COD reduction, but there's a threshold for which by adding more H_2O_2 the abatement of COD worsens. Based on the most significant factors (x_1 and x_1^2), a quadratic model for COD removal from wastewater was identified:

$$COD_{removal}(\%) = 84.74 + 12.2 x_1 - 5.62 x_1^2$$

The goodness of the model is confirmed by the scatter diagram of predicted against actual values, it indicates that the experimental and theoretical data are well correlated ($R^2 = 0.96$). Based on the determined quadratic model the optimal H₂O₂ concentration to maximize the removal of COD (91.38%) has been calculated to be 15.45% v/v (1.05 as coded value). For testing the model, a validation experiment was conducted using this optimized H2O2 concentration, resulting in a measured COD removal efficiency of 93.62%. The difference in terms of COD removal falls within the experimental error. This test confirmed the accuracy and reliability of the quadratic model in predicting the effectiveness of H₂O₂ concentration for COD removal.

Table 16 reported the water composition after the Fenton treatment and lime precipitation. The Fenton process enables the breakdown of organic substances into simpler organic compounds, precipitating in the sludge. Additionally, the metals in the solution (such as Fe and Cu) are precipitated as hydroxides in the sludge after adding lime. Therefore, as a result of the treatment, 190 kg of wet sludge is generated per cubic meter of treated wastewater.





Composition of the treated water (method: ICP-OES and HACH-lange)			
рН	7.2		
COD	457 mg/L		
Fe	< 0.1 mg/L		
Cu	< 0.1 mg/L		

Table 16. Composition of wastewater after treatment.

The quality of the treated water, which would be within the limits for a direct discharge into the sewer, demonstrates its suitability for direct reuse in hydrometallurgical processes, reinforcing operational efficiency and sustainability from a water use perspective. This way, the process can be performed by reducing the water footprint according to a MLD approach.

2.1.2 Process analysis at pilot scale

This paragraph illustrates the process flow diagram and provides a full description of the various unit operations, based on the validation test conducted at the pilot scale. Additionally, the description of the mass and energy balances, as well as the main results in terms of silver recovery and the purity of the obtained powder are included.

The flowsheet of the developed process is shown in Figure 11. The hydrometallurgical process aimed at recovering silver from in-mold electronics (IMEs) according to a minimal liquid discharge (MLD) approach.









The hydrometallurgical process includes a two-step leaching (solid-liquid extraction) for the dissolution of silver and the subsequent recovery of silver from the solution by electrodeposition. The leaching solution is composed of thiourea (20 g/L) and ferric sulfate (6 g/L as Fe^{3+}) in a sulfuric acid media (0.2 mol/L). Thiourea can bind with precious metals such as Ag by coordination bonds since it has a lone pair of electrons on nitrogen and sulfur atoms. As thiourea is not stable and decomposes easily in an alkaline environment, the reaction requires an acidic media. Ferric ions are used as the oxidizing agents to ensure the dissolution of silver and the formation of the thiourea-Ag complex. The following reaction occurs:

$$Ag + 3CSN_2H_4 + Fe_2(SO_4)_3 \rightarrow Ag (CSN_2H_4)_3SO_4 + 2FeSO_4$$
(3)

The second step of leaching is conducted by reusing the solution obtained by the first step with a make-up of chemicals based on the amount consumed, measured by titration. Specifically, for the second step, 5.4 g/L of thiourea and the entire quantity of Fe^{3+} (6 g/L) have been added to the leach liquor, instead is not necessary a make-up of sulfuric acid. The leach liquor solution after the two steps of leaching, in which 84.4% of silver has been dissolved, is sent to the electrodeposition for silver powder recovery.

Electrodeposition occurs at the following operative conditions: voltage = 1.2 V, current density 50 A/m², silver as cathode material, and titanium coated by a mixed oxide as anode. The silver metal powder has been recovered with a purity of 98.57%; the main impurities are due to iron (0.26%), copper (0.10%), and calcium sulfate (1.07%). The following reaction occurs for the reduction of silver into metal during the deposition on the cathode:

$$2(Ag (CSN_2H_4)_3)_2SO_4 + 2H_2O \rightarrow 4Ag + O_2 + 2H_2SO_4 + 12CSN_2H_4$$
(4)

The discharged silver solution is not wasted, but rather, it can be reused in a new cycle of the process, promoting a sustainable approach. This is made possible by the partial regeneration of thiourea, and the increase of free acidity as shown in the reaction, with a make-up of chemicals to perform the first leaching step of the second cycle. The addition of chemicals to the solution is the following: thiourea 1.5 g/L, Fe^{3+} 6 g/L.

The process can be conducted in this way for three cycles, significantly reducing the freshwater use, with an overall silver recovery of 82.9%. The average silver dissolution rate obtained was 84.2%, while the recovery of silver from the leach liquor by electrodeposition was 98.4%.

The wastewater treatment section is a crucial part of the process, ensuring that the water used is treated to the highest standards. It includes a Fenton treatment to decompose organic substances, and a lime treatment for an overall reduction of COD of 94% and of iron that exceeds 99%. This ensures that the water obtained from the wastewater treatment section is of high quality, with 70% of it being reused in a new batch of the hydrometallurgical process, and the rest being discharged in sewerage as the COD and metal content are below the required limits. This way, water consumption was reduced to 464 kg to treat 1 ton of IMEs. The water footprint equals 60.3 kg of water/kg silver product.

Table 17 shows the efficiency of the process in terms of silver recovery both for the leaching and the electrodeposition. The silver recovery in the leaching is 84.2%, it has been calculated as an average of the three cycles, it can be observed that in the cycles after the first in which the solution was reused with a make-up of reagents, there is no loss of efficiency. The





electrodeposition efficiency as silver recovery was 98.4%, the calculations are explained in detail in paragraph 2.1.1.2. Therefore, the overall silver recovery of the process was 82.9%.

Results of the validation pilot plant test for the recycling of Ag from IME				
Cycla na	Ag recovery, %			
Cycle, no.	Leaching 1 st	Leaching 2 nd	Electrodeposition	
1	66.1	84.4	65.1	
2	64.2	83.4	73.1	
3	65.1	84.8	96.1	
Batch (1+2+3)	65.1	84.2	98.4	
		82.9%		

Table 17. Results obtained by the validation pilot plant test, silver extraction yields.

Table 18 presents the mass balance based on the results obtained in the pilot-scale validation process. The calculations refer to the processing of a ton of IME. The average initial concentration of silver in the IME samples was $0.93\% \pm 0.37\%$ (the chemical composition is reported in D5.4).

Input, kg		Output, kg		
solid (IME)	1000.0	dry solid/secondary product	984.0	
water	464.3	humidity	47.1	
thiourea	130.7	silver powder	7.7	
ferric sulphate	449.6	treated water to sewerage	1189.3	
sulfuric acid, 50 %	131.5	wet sludges	666.7	
hydrogen peroxide, 30%	571.7	-	-	
lime, 10%	147.2	-	-	
	2894.8		2894.8	

Table 18. Mass balance of the process tested at pilot scale for the treatment of 1 ton of IME.

The water use was significantly reduced when compared to the lab-scale test (D5.4). This was made possible by introducing a wastewater section that enables the production of treated water with quality characteristics suitable for reuse in subsequent cycles to prepare leaching solutions. The leaching operations aimed at dissolving silver involved the use of thiourea, ferric sulfate, and sulfuric acid. On the other hand, hydrogen peroxide and lime were the reagents used in the wastewater treatment section.

Below is a detailed description of the outputs of the process, this allows us to best assess its economic and environmental sustainability. The solid residue (dry solid/secondary product) consists essentially of the polymeric substrate on which the silver ink is printed. The polymeric layer is not affected by the chemicals during the hydrometallurgical recovery of silver. This solid residue can be considered as a secondary product, TNO has conducted some tests for the recycling of polycarbonate reaching recoveries of the order of 80%. Some results are reported in D6.3. Table 19 shows the composition.





Solid residue – method (ICP-OES analysis)			
polycarbonate or other plastics	not determined		
Ag	0.15%		
Fe	0.04%		
Cu	0.03%		

Table 19. Composition of the dry solid/secondary product.

In Figure 12, samples of IME from which silver has been recovered, i.e. the solid residue of the process, are shown.





Figure 12. Dry solid/secondary product photographic aspect.

The silver powder obtained by the process tested at the pilot scale has been subjected to ICP-OES analysis after the chemical attack and to XRD analysis to evaluate the silver purity and its form beyond the impurities. Table 20 shows the silver powder composition and Figure 13 the XRD spectrum which shows that silver is in its metallic form.

Table 20. Silver powder composition	Table 20.	Silver	powder	com	position.
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Silver powder quantitative chemical analysis (method: ICP-OES)			
metal/salt wt. %			
Ag	98.57		
CaSO ₄	1.07		
Fe	0.26		
Cu	0.10		







Figure 13. Silver powder XRD spectrum and its photographic aspect.

The wastewater section is composed of a Fenton process where only hydrogen peroxide is used since the already high iron content of wastewater and a subsequent stage of precipitation with lime allows for obtaining treated water with a range of pH close to the neutrality and a sludge of calcium in which the pollutants are transferred.

In Table 21 the composition of the treated water and the sludges of calcium are reported.

Wastewater treatment section				
Treated water – method (ICP-OES analysis)				
рН 7.2				
COD	457 mg/L			
Fe	< 0.1 mg/L			
Cu	< 0.1 mg/L			
Ag	< 0.1 mg/L			
Dry sludges (XRF analysis)				
CaSO ₄ 63.6%				
FeSO ₄	34.5%			
CuSO ₄	0.9%			

Table 21. Outputs of the wastewater treatment section.

The water obtained from the treatment meets certain requirements in terms of its qualitative characteristics. These requirements ensure that the water can either be reused in the recycling process or can be safely discharged into the sewerage system. Specifically, the water has a COD level below the limit of 500 mg/L as well as the metals below their limits.

Concerning the sludges they are mainly composed of calcium sulphate because of the addition of lime to regulate pH and precipitate metals after Fenton, and of iron sulphate because of the high content of iron in the wastewater since is used as a reagent in the leaching operation. Based on some preliminary investigations, it has been found that this type of sludge can be disposed of at approximately $80 \notin kg$.





Economic evaluations on the recycling of IME are now conducted based on the results obtained on the validation test performed at the pilot scale. Table 22 shows the chemical consumption and their costs for the treatment of 1 ton of IME, by also including the wastewater treatment section.

Chemical	Amount, kg	Cost per unit, €/kg	Cost, €
water	464.3	0.0015	0.7
thiourea	130.7	1.00	130.7
ferric sulphate	449.6	0.30	134.9
sulfuric acid, 50 % 131.5 0.13		17.1	
	283.4€		
hydrogen peroxide, 30%	571.7	0.35	200.1
lime, 10%	147.2	0.015	2.2
wa	202.3€		
entire process fo	485.7€		

Table 22: Chemical consumptions and costs for the treatment of 1 ton of IME.

In Table 23 the energy consumption per each stage of the process has been reported. They consider the pumps for the loading of the reagents, the stirring for the preparation of leaching solutions, the pumps to transfer the solutions, the power supply for the electrodeposition, and the recirculation pump. The main contribution comes from electrodeposition which has an energy consumption of 5.3 kWh per kg of recovered silver.

Operation	kWh	€/kW	Cost, €
Leaching	9.5	0.40	3.8
Electrodeposition	40.8	0.40	16.3
Wastewater treatment	4.9	0.40	2.0
Entire process	60.1	0.40	24.0€

Table 23: Energy consumptions and costs for the treatment of 1 ton of IME.

OPEX and revenue are estimated for treating 1 ton of IME. Specifically, the costs for reagents of both the hydrometallurgical process and the wastewater treatment section, energy consumption, and treated water that could potentially be reused or discharged into sewerage systems, are considered. Regarding the solid residue of the process, which is primarily a polymeric layer with some residual silver, some tests have been conducted in the ambit of the project for recycling polycarbonate by TNO. Since these tests, although gave promising outcomes, are in the research phase and it is still difficult to identify an end user for the recycling of plastics and to estimate possible economic agreements, it has currently been classified as a non-cost, non-revenue item pending specific assessments. Costs relating to operators are not taken into account as they are closely linked to business choices also based on the number of shifts of work.

As regards the estimate of revenue is to be considered the product consisting of metal silver powder. The amount recovered per ton of processed IME and its purity was considered in the revenue estimate. To assess the economic value of silver and avoid making economic





considerations corresponding to fluctuations in market value was considered an average value of the last 5 years, as shown in Figure 14.

Year	Average Closing Price	Year Open	Year High	Year Low	Year Close	Annual % Change
2024	\$24.19	\$23.79	\$28.88	\$22.09	\$28.68	20.54%
2023	\$23.40	\$23.96	\$26.06	\$20.01	\$23.79	-0.72%
2022	\$21.76	\$22.81	\$26.90	\$17.83	\$23.96	2.64%
2021	\$25.14	\$27.36	\$29.42	\$21.49	\$23.35	-11.55%
2020	\$20.69	\$18.05	\$29.26	\$11.77	\$26.40	47.44%

Silver Prices - Historical Annual Data

Figure 14. Silver prices (\$/ounce) in the last five years. Source: Macrotrends [4].

Therefore, based on these data, the average silver price in the last five years is 23.0 \$/ounce, corresponding to 763.8 €/kg.

As regards purity, the economic value of silver according to purity in the range of 50 - 100%, updated on 22 April 2024, is shown in the table in Figure 15. The percentage of the economic value of each purity compared to that of 100% pure silver has also been calculated. In the chart, the indicators show the purity values as a function of the percentage of the economic value of silver at Ag 100%; the dotted line indicates a potential trend. Given that the purity of silver recovered by the hydrometallurgical process is 98.57% it was estimated from this graph an approximate depreciation compared to 100% Ag purity. Thus, a purity of 98.57% according to this estimate corresponds to 86.75% of the economic value of 100% pure silver. So, we have a depreciation of just over 13%. Referring to the average price of silver for the last 5 years calculated earlier, it can be considered that the silver recovered by the process has an economic value of 662.59 €/kg.



Figure 15. Silver prices as a function of purity. Source: Bullion By Post [5].

Based on these considerations, Table 24 reports the OPEX and revenues for the treatment of 1 ton of IME.





Item			Cost, €	Revenue, €
Chemicals	details are repoi	rted in Table 22	485.7	-
Energy consumption	details are repor	rted in Table 23	24.0	-
Treated water to sewerage system	1189.3 kg 0.5 €/m³		0.6	-
Wet sludges	666.7 0.08 €/kg		53.3	
Secondary product management	984.0 kg	0.0 €/kg	-	-
Silver powder (98.57%)	7.7 kg	662.59 €/kg	-	5101.9
prof	+ 453	8.3€		

Table 24: OPEX and revenues for the treatment of 1 ton of IME.

Thus, this process is also feasible from an economic point of view, since for each ton of processed material it can generate a profit of 4538.3 €. Further insights are still pending on solid waste management.

2.1.3 Discussion

IME is an innovative technology and significantly different from conventional electronics in which components are reflow soldered onto printed circuit boards. This solution, shortly, could partially replace flat and rigid PCBs by adopting functional surfaces that are more cost-effective, lighter, and visually appealing. The use of IME is certainly worth exploring as it could have a significant impact on the automotive industry.

Specific meetings were held between UNIVAQ, TNO, WALTER, and POLIMI to investigate themes related to the IME market analysis. Predicting the availability of IME is crucial for defining the correct size of the hydrometallurgical silver recycling plant. To achieve these objectives, it's necessary to estimate the amount of IME placed in the market and define their average lifetime to predict when they will become a 'waste', which would be the recycling plant's input. The global 10-year market forecast is shown in Figure 16.







Figure 16. IdTechEx forecast for the automotive console IME market [6].

The global IME market is rapidly growing due to rising demand in automotive, consumer electronics, and healthcare applications, offering enhanced performance, product aesthetics, and reduced costs.

The market value is expected to reach USD 2,358.09 million by 2033, with a CAGR of 28.83% from 2023 to 2032 [7]. Some of the major companies involved in this market include DuPont de Numours, TactoTek Oy, Golden Valley Products, Nissha Co. Ltd., Butler Technologies, GenesInk,





YOMURA, InMold Solutions, Eastprint Incorporated, and DuraTech Industries. IME technology is widely used in the automotive industry to produce various components such as structural parts, entertainment systems, and interior and exterior components. The technology involves integrating electronic components such as sensors and displays into injection-molded parts and finished assemblies.

Silver currently appears to be one of the key elements for the energy transition, given its wide use in photovoltaic panels. In addition, battery electric vehicles (BEV) will depend heavily on silver. A Silver Institute report highlighted that BEVs contain up to twice as much silver as ICEpowered vehicles [8]. Each BEV contains between 25 and 50 grams of silver, depending on the model. The electrical and thermal conductivity of silver makes it an ideal material as part of an automobile battery. It is also ideal for use in BEVs because it's non-toxic. Charging points and charging stations are also expected to demand a lot more silver. A charging module is usually composed of switches, transformers, relays, and connectors. Most of the contacts in this apparatus are made of silver. The sector's demand for silver is estimated to rise to 88 million ounces in five years as the transition from traditional cars to BEVs accelerates. Others estimate that by 2040, electric vehicles could demand nearly half of the annual silver supply. Silver is primarily used in the manufacture of jewelry (21-25%) and silverware (5-8%), photography (4-5%), photovoltaics (11-13%), and electronic parts (6-7%), but it is also widely used in the automotive industry (8-9%), catalysts (7-8%), batteries (7-8%), brazing and soldering (7-8%), glass (6-7%) and other parts, bearings (6-7%), and medicine (4%). The silver ore market size is expected to grow sharply in the next few years. It will increase to \$11.4 billion in 2028 at a compound annual growth rate (CAGR) of 8.8% [8].

UNIVAQ has developed a new hydrometallurgical process for recycling silver from IME, which has been successfully tested at a pilot scale using the reconfigured hydrometallurgical pilot plant. The hydrometallurgical process for the recycling of silver from IME has been validated at a pilot scale. Results confirmed that the implemented process could generate a profit, and it consumes 464.3 kg of freshwater per ton of IME, which is low if compared to other conventional hydrometallurgical processes [1]. This way, a smart route for the recovery of silver has been enabled according to a circular economy approach by reducing its supply from mineral resources. The process includes reusing solutions from which silver is recovered and introducing a wastewater section that allows minimized freshwater use. The main innovative aspect is a partial regeneration of thiourea that occurred during the electrodeposition process; this way, chemical consumption has been reduced. As a result, the operating costs are significantly lower when compared to other hydrometallurgical processes. **UNIVAQ has submitted a patent proposal for this innovative recycling method.**

Currently, it is not feasible to build an industrial silver recycling plant as the availability of IME is limited. However, the technology developed is also suitable for recycling silver from photovoltaic panels. Although a control phase is still necessary to dose reagents appropriately based on the input material. In the future, when more IME becomes available, a combined plant could be developed that can recover silver from both photovoltaic panels and IME. With the development of this hydrometallurgical technology, it is now possible to construct a plant capable of processing photovoltaic panels and incorporating IME when such materials are available.

To achieve the goal of being carbon-neutral by 2050, Europe needs to move from a linear 'brown' to a circular, green economy. This circular society strategy is usually seen in Europe as an





incubator for economic growth and development while also lowering carbon emissions and accomplishing the green transition. A successful pan-European transition to a circular society is dependent on a consistent and sustainable supply and management of raw resources. Raw, processed, and advanced materials derived from primary (mines) and secondary (recycled) sources constitute the foundations of the circular economy and society. The circular society reduces the loss of unused materials along the value chain. End-of-life products are seen as a resource that may be re-entered in the market. Industry and consumers simultaneously support a 'closing the loop' approach.

For this purpose, during the project activities, TNO suggested investigating the circularity of silver by exploiting the expertise of GENESINK (advisory board member) in the formulation of silver ink. The objective was to use silver powder recovered by hydrometallurgical processes from UNIVAQ on a pilot scale, as a precursor for the formulation of new ink (GENESINK) that could then be reused by TNO in the production of new IME, in this way closing the loop completely (Figure 17).



Figure 16. Silver circularity in IME recycling.

The silver powder utilized for the ink formulation was obtained from UNIVAQ hydrometallurgical pilot plant preliminary tests with 64% silver grade and copper as the main impurity.

GENESINK acquired Ag powder and attempted to create an ink that was similar to a previously used formulation. As UNIVAQ supplied them with a limited quantity of the silver powder (about 15 grams), they had to use the entire amount to prepare the ink. After formulating the ink, it separated into two layers, with agglomerates settling at the bottom and solvents on top. They observed that the ink had a high viscosity due to the agglomerates. So, they were unable to obtain conductive and smooth deposits. They experimented with two different spin coating speeds and subjected the ink to ultrasound, but the deposit remained granular and nonconductive. Below are reported some explanations that potentially could have caused this issue that may affect the ink's characteristics and quality:

- Impurities in the Ag powders.
- The particle size of the powders was higher.
- Minimal amount of powder used.





UNIVAQ has ended the availability of IME provided by TNO, which means that further testing cannot be carried out. The pilot tests on the optimized process were conducted on smaller amounts of IME. Consequently, the powder obtained at a silver purity of about 98.6% was limited to only 5-6 grams. Therefore, GENESINK cannot carry out further investigations. By conducting these tests, we are taking the first crucial step towards achieving the goal of silver circularity in IME.

2.2 Recycling of printed circuit boards

The paragraph below outlines the outcomes of the pilot tests conducted on the reconfigured plant for recycling combineter PCBs.

UNIVAQ has identified the need for an initial stage of disassembly for specific SMDs and has developed two hydrometallurgical routes based on laboratory-scale activities (D5.4 – ANNEX 3). These routes have allowed for maximization of yields, particularly that of gold, which is the element that contributes most to the intrinsic economic value (IEV) of PCBs.

Specifically, one route was intended for the treatment of the board with some residual SMDs that, after grinding to obtain a powder below 2 mm, was used to recover copper, tin, gold, and silver starting from Gold-REC 1 UNIVAQ patent. Palladium was present in a too low concentration to hypothesize a recovery. Factorial experimentation allowed us to adapt the process to this specific material and to maximize metal extraction yields by minimizing chemical consumption, also considering an MLD approach. The main modification was related to adding one more leaching stage with a better use of hydrogen peroxide. Thus, for the pilot plant tests, the main purpose was to study the scale-up of the process, evaluate the possibility of further increasing the yield of gold that was probably depressed due to the methods of grinding, and study the reuse of water thanks to the introduction of a wastewater treatment section.

UNIVAQ provided datasheets with the procedure to obtain the powders after removing some specific components for material requests to SEAT, ILSSA, and POLLINI. The minimum amount needed to conduct at least a couple of pilot scale replicas was 10-15 kg. Based on the weight of combimeter PCBs needed at least 100 cars to supply the required amount. ILSSA was the only supplier that met this request, providing 11 kg of PCB powders below 2 mm after removing some specific SMDs. Since ILSSA is a dismantler, these powders have been obtained from different car models and not only from SEAT car models that had been studied on a laboratory scale (Task 5.3 and 5.4).

The second hydrometallurgical route was intended for the recycling of specific SMDs with a high concentration of gold that was mainly on the surface such as in the case of gold-plated components. Specifically, the components were golden wired, connectors and small PCBs. This route was investigated at the lab-scale starting from the Gold-REC 2 UNIVAQ patent. Also, in this case, UNIVAQ asked for these components SEAT, ILSSA, and POLLINI. The minimum amount to perform a test on a pilot scale was approximately 5 kg. The issue was that the supply of these components was not easy since they are about 5% by weight of PCB; therefore, to obtain 5 kg would need almost 700 cars, by only focusing on the combimeter PCB. POLLINI provided around 50 grams of these components, but because of the limited amount, it was not possible to conduct the test at a pilot scale. However, UNIVAQ has created a prototype plant on a laboratory scale, suitable for small quantities but with equipment manufactured in the same way as those of a pilot-industrial plant, with the aim of validating this process and evaluating potential issues. Since the results for the recycling of these components, obtained during Task 5.4, showed that





in some cases, metal recovery was not satisfactory, further studies were also conducted to improve the leaching efficiency.

The purpose of this activity is to validate the recycling of PCBs in the automotive sector by finalizing the two hydrometallurgical routes and confirming the technical-economic feasibility after pilot/prototype plant tests.

2.2.1 Pilot tests

This section presents the findings of tests on the recycling of combimeter PCBs through hydrometallurgical processes after disassembling specific SMDs. POLIMI activities in Task 6.1 fully investigated the disassembly process using COBOT technology. Consequently, two subsamples were obtained from the initial PCB: one included the base of the board with some components such as ICC, which was ground to a powder of 2mm, and the other had gold-plated SMDs, such as connectors, golden wires, and small PCBs. The first route, called Gold-REC 1, was investigated by testing the process on the reconfigured hydrometallurgical pilot plant, while the second route, named Gold-REC 2, was studied by adopting the prototypal plant. The two hydrometallurgical routes are shown in Figure 17.



Figure 17. Recycling of PCBs according to the two hydrometallurgical routes.

This figure also shows that without the disassembly operation, the gold extraction yield by applying the Gold-REC 1 process will be significantly lower. It depends on the presence of some components that must be removed from the board because if ground with all the board during the hydrometallurgical treatments, they would inhibit the dissolution of precious metals. These components are electromagnets, transducers, aluminum capacitors, and crystal oscillators. Additionally, in the hydrometallurgical process, a high copper content in the solid would increase the acid consumption to dissolve the copper and ensure the subsequent recovery of the precious metals. Thus, it also adversely affects operating costs and environmental impact. This is the case for components such as electromagnets that have a copper coil, as well as crystal oscillators. In addition, the presence of steel and aluminum negatively affects the dissolution of metals as they are reducing agents; this is the case for capacitors and transducers. Therefore, these




components are not suitable for a hydrometallurgical recycling process and should be treated to recover their valuable metals by thermal treatments.

2.2.1.1 Recycling of PCBs powders by Gold-REC 1

ILSSA supplied the necessary material for testing at the pilot scale, which was prepared according to the instructions provided by UNIVAQ. The first level of disassembly includes the operation to obtain the PCB from the dashboard, while the second level of disassembly involves the removal of some SMDs. As part of the treasure project, we focused on combineter PCBs only. To obtain about 10 kg of these powders, PCBs were dismantled from approximately 60 cars. Table 25 provides details about the sample preparation, times, and energy consumption.

Operation	Equipment	Time per car	Time per 10 kg
Disassembly - first level	manual with tools	8-12 min	10 h
Disassembly - second level	manual with tools	2–2.5 min	2 h 15 min
Grinding	roller shredder (7.5 kW)	n.a.	1 h 06 min

Table 25: Disassembly operation and sample preparation performed at ILSSA for pilot tests.

ILSSA has prepared this material on different types of models of cars that have to be managed, in some cases, and damaged vehicles. Disassembling the first level can be quite challenging, and based on ILSSA's estimates, it takes over 40 days to extract a ton of PCBs from dashboards. The second level of disassembly was made by ILSSA manually; they did not use heat to unsolder the components, and by reporting, the time taken to the preparation of one ton of PCBs would be about 9 days. This operation, however, could be automated by considering the advances obtained by POLIMI in the study of second-level disassembly through COBOT technology (D6.1). According to the available data, it appears that the process of preparing a ton of 2mm powder via the grinding operation requires a considerable energy consumption of about 750 kW/h, considering the power of the shredder used. Pictures of the roller shredder are shown in Figure 18.





Figure 18. Roller shredder used by ILSSA for sample grinding.

The powders supplied by ILSSA were characterized by UNIVAQ by performing a chemical attack using aqua regia on a representative sample, followed by quantitative analysis using ICP-OES. The results are presented in Table 26; the concentration of elements is reported as metals. The recovery rate is generally influenced by the compound in which the different elements are present in the initial material.





replications, n.	Au, g/t	Ag, g/t	Pd, g/t	Cu, %	Sn, %
1	24.5	122.2	9.5	6.87	0.33
2	19.0	92.8	8.9	7.56	0.55
3	22.7	194.7	11.5	9.67	0.27
4	25.4	145.6	6.5	7.19	0.31
5	18.3	167.5	8.3	11.24	0.42
average	22.0	144.6	8.9	8.51	0.38
std dev	3.2	39.4	1.8	1.88	0.11

Table 26: PCBs powders of ILSSA for pilot tests after removal of some SMDs.

The analyses show that the content of precious metals, copper, and tin is significantly lower than the powders used for laboratory tests from SEAT car models (D5.4 – ANNEX 3). Specifically, in the case of gold, the powders from combineter PCBs of SEAT models had an average value of 64.9 g/t with a maximum of 94.2 g/t for SEAT IBIZA IV. The concentration of these powders is also significantly lower for the other metallic values, as shown in the table above, even less than half as compared to the SEAT models. This change results in reducing the IEV by over 50%, from $8.66 \notin/kg$ to $3.75 \notin/kg$ compared to SEAT IBIZA IV, by considering the content of the elements in the above table. The main reasons for significantly lower concentrations have been hypothesized below:

- loss of part of the finest powders during the grinding phase
- high variability of the gold as a function of the various car models

The first issue can be resolved by intervening on the equipment used for grinding or by grinding the material in an enclosed environment to retrieve any finer powders that might have dispersed during the process.

The second issue is a crucial aspect that could impact the viability of the recycling process. Reducing the IEV of the material by half would affect the economic feasibility of the process. To ensure the sustainability and viability of the car recycling process, it is necessary to know the chemical composition of the car model in advance, especially the concentration of gold. This can be achieved by tracing electronic components used in critical parts of the car. As part of the project activities, UNI has developed a CEN Workshop Agreement with contributions from most of the partners, called "A methodology to improve the recyclability rate of strategic/critical metals from cars". The main objective of this agreement, from a recycling perspective, is to define material declaration requirements that allow us to determine the presence of specific electronic components in advance and thus avoid unnecessary disassembly efforts for models where recycling is not worthwhile.

Anyway, despite the lower content of the metals to be recovered, the pilot-scale tests were executed on the powders provided by ILSSA. These tests aimed to validate the reconfigurations carried out on the pilot plant (D5.4 – ANNEX 1) and assess if the technical issues, which were raised during the FENIX project, were mitigated due to the implemented changes. The purpose of these tests was to determine the technical feasibility of the reconfigured pilot plant as well as evaluate process efficiencies.

Figure 19 shows the flowsheet of the process for the hydrometallurgical treatment of the PCB powders for the recovery of gold, silver, copper, and tin.







Figure 19. Hydrometallurgical recycling of PCBs powders according to Gold-REC 1 process.

The process includes two-stage leaching sections: in the first, the dissolution of base metals, and in the second, the dissolution of precious metals such as gold and silver. In this way, the base and precious metals are efficiently separated in the leaching section. The efficiency of the first stage strongly affects the leaching efficiency of precious metals that occurs in the second stage. The first leaching stage is composed of three counter-current steps of leaching conducted by 1.8 mol/L sulfuric acid and 5-10% v/v of hydrogen peroxide according to the scheme shown in Figure 20. The addition of one more step by reducing the concentration of hydrogen peroxide with respect to the Gold-REC 1 patent was one of the main results obtained during the lab-scale optimization.



Figure 20. Counter-current multi-steps base metals leaching.





The selective recovery of metals from the solutions in which they have been dissolved occurs as described below. Tin is recovered from the pregnant solution by precipitation with a polyamine in the form of metastannic acid, which can be thermally treated to obtain tin oxide as a final product. Copper remains in the solution and is recovered by electrodeposition. The second leach liquor solution, rich in precious metals, obtained by leaching with thiourea (20 g/L), Fe^{3+} (6 g/L), and 0.2 mol/L sulfuric acid is then subjected to electrodeposition for the recovery of gold and silver, which based on the experimental tests, cannot take place selectively. Therefore, a refining step is necessary to dissolve silver from the gold-silver alloy to increase gold purity. Silver has been recovered from the acid solution as chloride.

The equipment used for the pilot tests is described briefly below. The chemical reactor for leaching operations has been selected based on the type of material, which is a fine powder. The selected reactor (R102) has a capacity of 100 litres and is built in polypropylene. It was added during the reconfiguration of the pilot plant and features an agitator that reaches almost the bottom of the reactor. This design allows for better mixing of the suspension and facilitates the phase of powder discharge during filtration. Additionally, due to clogging issues experienced with reactor R101 during the previous European project FENIX, a bag filtration system was also installed. To ensure optimal performance, the reactor R102 was positioned slightly higher than the filter. The chemical reactor R102 was used once again to recover tin through precipitation, while the copper recovery was tested via electrolytic cell CE102. Unfortunately, we were unable to test the recovery of gold and silver due to their very low concentrations in the initial powders (Table 26) and solutions, which greatly influences the efficiency of the electrodeposition process. It is important to note that the concentration of metals to be recovered plays a critical role in the efficiency of the electrodeposition process.

Extraction yields were determined by also measuring the residual concentration of the metals of interest in the solid residue. This helped reduce errors related to sample representativeness.

The pilot test consisted of the following operations performed in the reconfigured hydrometallurgical pilot plant:

- 1. Prepare the leaching system in the chemical reactor R102.
- 2. Load PCBs powders into the chemical reactor R102.
- 3. Add hydrogen peroxide at different times during the reaction.
- 4. Allow for the chemical reaction to occur in R102.
- 5. Filter by using the bag filter and discharge the leach liquor into a tank.
- 6. Repeat steps from 1 to 5 three times to complete the base metals dissolution.
- 7. Prepare the leaching system in the chemical reactor R102.
- 8. Load the solid residue into the chemical reactor R102.
- 9. Allow for the chemical reaction to occur in R102.
- 10. Filter by using the bag filter and discharge the leach liquor into a tank.
- 11. Load the base metals-rich liquor in R102 and add the chemical for tin precipitation.
- 12. Allow for the chemical reaction to occur in R102.
- 13. Filter by using a cartridge filter and discharge the final leach liquor into a tank.
- 14. Recover the metastannic acid powder from the cartridge filter.
- 15. Load the leach liquor obtained by step 13 to the electrolytic cell CE102.
- 16. Set the rectifier voltage.
- 17. Begin the electrodeposition stage.
- 18. Discharge the solution into a tank and recover the cathode with the copper deposit.





The following operating conditions were used for leaching base metals: a solid concentration of 15% wt./v (10 kg in 67 litres), 1.8 mol/L H₂SO₄, 5% v/v H2O2 (30% wt./v), stirring at 200 rpm, and a duration of 1.5 hours. This process was repeated three times for optimum efficiency, with hydrogen peroxide added in multiple dosages during the reaction. For the precious metal stage, the operating conditions were as follows: solid concentration 10% wt./v, thiourea at 20 g/L, Fe3+ at 6 g/L, 0.2 mol/L H2SO4, stirring at 250 rpm, and a duration of 1 hour.

The results of the dissolution yields obtained by the pilot test for the base metals and precious metals leaching are reported in Table 27.

Leaching step	Au, mg/L	Ag, mg/L	Cu, mg/L	Sn, mg/L			
1 – base metals (1 st)	0.0	0.3	9425	527.5			
2 – base metals (2 nd)	0.0	0.0	1918	16.4			
3 – base metals (3 rd)	0.0	0.0	1257	7.4			
3 – precious metals	2.3	16.4	38.1	1.1			
	reco	overy yields, %					
1 – base metals (1 st)	0.0	1.2	74.2	93.0			
2 – base metals (2 nd)	0.0	0.0	15.1	2.9			
3 – base metals (3 rd)	0.0	0.0	9.9	1.3			
3 – precious metals	80.5	89.1	0.3	0.2			
remained in the solid residue	19.5	9.7	0.5	2.6			
	Au, %	Ag, %	Cu, %	Sn, %			
recovery in the	80 5	80.1	99.2	97.2			
correct step	80.5	05.1	55.2	57.2			
summary							
Solid	wt	. %	Au, g/t				
Feed	10	0.0	22	.2			
Solid residue	78	3.1	5.	5			

Table 27: Summary of results for the leaching operations on PCB powders at pilot scale.

The results achieved were satisfactory, with some elements even exhibiting higher extractions compared to the results obtained at the lab scale (D5.4 – ANNEX 3). For instance, in the case of gold, extraction yields of up to 70% were obtained during laboratory tests. With the same operating conditions, a pilot-scale increase of about 10% was achieved, resulting in a gold dissolution rate of 80.5%. The extraction of silver was also confirmed, with a dissolution rate of 89%. Furthermore, copper and tin extractions were slightly higher, with 99% and 97%, respectively, as compared to 95% and 96% obtained during the lab-scale tests.

Given the result obtained, further tests were also carried out on a laboratory scale on the same material supplied by ILSSA which showed similar yields to those reported in Table 27. To investigate the reason for the increase in yield, a laboratory test was conducted on the SEAT IBIZA 4-generation PCBs. The material was taken from another dashboard, and a new model of Retsch cutting mill (SM300) was used to obtain 2 mm powder. The results of this test were similar to the pilot scale results presented in Table 27. It was discovered that the lower yields obtained from previous experiments at the lab scale, as reported in D5.4 - ANNEX 3, were likely due to the method of grinding used. This affected the degree of liberation of the metal particles of interest, regardless of their grain size. In fact, an older model of a cutting mill was used for the lab-scale experimentation (Task 5.4).





In addition, leaching operations carried out on a pilot scale made it possible to test the equipment added with the reconfiguration of the plant and it was therefore confirmed that there was no clogging during the filtration for the separation of the solid solutions in which metals have been dissolved.

The leach liquor solution, 65 litres, obtained by the first step of the base metals leaching has been loaded in the chemical reactor R102 to investigate the precipitation of tin by adding polyamine, a cationic flocculant, that was firstly prepared by diluting it with water to a concentration of 10% wt./v. The operative conditions were flocculant (10% wt./v) 2.5 mL/L, 75 rpm of stirring, and 30 minutes for the precipitation. Table 28 shows the obtained results.

Table 28: Results for the recovery	of metastannic acid	I from the leach liqu	or solution.
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Tin recovery	Sn before the treatment, mg/L	Sn after the treatment, mg/L	Sn recovery, %
Solution from the first step of base metals	527.5	30.8	94.2
leaching			

Approximately 90 grams of metastannic acid powders were collected after performing the filtration using a 10 μ m porous nylon cartridge filter. The laboratory scale efficiency was confirmed by achieving 94.2% recovery of tin. The solid was subjected to a 1 hour of thermal treatment in a furnace with an oxidant environment to produce tin oxide as the final product. Figure 21 shows a picture of the tin oxide powders.



Figure 21. Tin-oxide powders obtained from the pilot test.

The tin oxide powder was chemically attacked with aqua regia and analyzed by ICP to evaluate its purity. The analysis confirmed that the tin oxide had a purity of 99.1%. The primary impurity detected in the powder was 0.7% copper oxide, alongside some residual amounts of polyamine. The tin oxide purity was almost 2% higher compared to that obtained on a laboratory scale, which was more affected by experimental errors where since the lower amount was obtained.

After recovering the tin, the remaining solution was sent to the electrolysis cell identified as CE102 to recover copper via electrodeposition. The operation has been studied by using one anode made of titanium coated with mixed oxides and a copper cathode where copper deposition from the solution occurred. The test was conducted by maintaining the operative conditions already investigated at the lab scale, but to keep the current density to 250 A/m², the voltage was slightly increased from 2.0 V to 2.3 V. Figure 22 shows pictures of the operation





conducted at the reconfigured pilot plant. In the left picture, you can see the electrolytic bath during the electrodeposition process. On the right side, there is the copper plate with the recovered copper on its surface.





Figure 22. Copper electrodeposition from powders of PCBs. Left side: electrolytic cell during the operation; right side: the obtained copper deposit on the cathode.

Copper recovery from the solution as a function of current efficiency at different times is shown in Figure 23.



Figure 23. Copper electrodeposition at pilot scale, the copper recovery vs current efficiency as a function of time.

It has been confirmed that a one-hour electrodeposition process, under conditions that maintain a current efficiency of at least 85%, is sufficient for achieving high copper recovery. In pilot scale testing, a copper recovery rate of 98.1% has been achieved with an energy consumption of 2.3 kWh per kilogram of recovered copper. As a result of the reaction that takes place at the anode during electrodeposition (5), the concentration of free acid in the solution increases. To measure this effect, the concentration of sulphuric acid in the solution was measured before and after the electrodeposition by titration. The results confirmed that there was an increase in concentration from 1.0 to 1.3 mol/L.





$$H_2 O \rightarrow H^+ + O H^- \rightarrow 0.5 O_2 + 2H^+ + 2 e^-$$
 (5)

An analysis was conducted on the metallic copper powder obtained after electrodeposition. The analysis used ICP-OES and was carried out after the metals were solubilized by acid chemical attack. The results showed that the copper powder had a purity level of 99.4%. The analysis also revealed the presence of impurities, including 0.3% iron, 0.2% nickel, and 0.1% zinc.

As mentioned earlier, the gold and silver recovery tests from the solution in which the precious metals were dissolved had high dissolution efficiencies. However, due to the low concentration of gold in the initial material, it wasn't possible to carry out the tests. This is because the electrodeposition process of gold is strongly influenced by its concentration, which was only about 2 mg/L. If the initial gold concentration was at least 80 g/t as determined for SEAT LEON II and SEAT IBIZA IV, then a gold concentration of 10 mg/L would be obtained in the solution. This would allow us to effectively test the electrodeposition of gold at a pilot scale.

From a richer material, however, other electroplating tests for gold and silver recovery have been conducted and allowed the following simultaneous recoveries: 98% for the Au and 76% for the Ag, working at a voltage of 1.5 V for about 2h. This treatment requires an energy consumption of 13 kWh/kg of product (dorè) recovered.

The wastewater from the pilot plant tests, resulting from leaching base metals and precious metals after electrodeposition treatments, was studied to explore the possibility of recovering additional metallic values of interest and treating it to obtain water with suitable quality characteristics for reuse.

A chemical cementation treatment has been studied to recover the remaining copper from wastewater resulting from the leaching of base metals. This treatment involves adding metallic iron (0.5 g/L) based on the reaction's stoichiometry to recover almost all the copper from the solution. Subsequently, treating the solution with lime until neutrality is achieved results in treated water suitable for reuse. However, this process generates about 190 kg/m³ of wet sludge that needs to be disposed of. Instead, the wastewater generated from leaching precious metals and subsequent electrodeposition contains thiourea, an organic substance used as a reagent. Investigating a chemical oxidation treatment to reduce the COD level below the reuse or sewage discharge limits is essential. The Fenton process was used to conduct tests, resulting in a 97.6% reduction in COD. Subsequent treatment with lime made the water suitable for reuse while producing wet sludge for disposal.





2.2.1.2 Recycling of electronic components from PCBs by Gold-REC 2

The second hydrometallurgical route was designed to recycle certain SMDs and other electronic components with a high concentration of gold on their surface, such as gold-plated components. As mentioned earlier, these components were supplied by POLLINI and provided around 50 grams of them from various car models, predominantly from FIAT cars. Because of the limited amount of components, tests have been performed by using a specific prototypal plant that has been realized to properly evaluate the scale-up of the process, even with low quantities. This prototype was created using the same equipment and materials as the reconfigured hydrometallurgical pilot plant but on a smaller scale. The cylindrical polypropylene reactor contains a porous septum to retain non-powdered materials, similar to the chemical reactor R103. The pneumatic diaphragm pump allows for proper testing of the filtration operation. Figure 24 shows some pictures of the prototypal plant.



Figure 24. Prototypal plant used for testing Gold-REC 2 process on the electronic components. Figure 25 shows photos of the components on which this treatment was investigated for the recovery of metals.



Figure 25. Electronic components provided by POLLINI. a) connectors; b) golden wires; c) small PCBs.

Specifically, the electronics components were connectors of different sizes, golden wires, and small PCBs.

After obtaining low yields of gold extraction in previous tests (D5.4), it was concluded that the issue was likely due to insufficient exposure, particularly in the case of pin connectors. Therefore, it was decided to include a preliminary grinding process of up to 1 cm to improve the exposure and increase dissolution yields. Then, the process has been investigated according to the flowsheet, named Gold-REC 2, shown in Figure 26.







Figure 26. Hydrometallurgical recycling of electronic components from PCBs according to the Gold-REC 2 process.

The process involves an initial leaching. In this treatment, both precious and base metals are dissolved using a combination of hydrochloric acid, hydrogen peroxide, and acetic acid. All the main metal values are then selectively recovered from the solution by methods like precipitation and chemical cementation.

Firstly, gold is recovered from the solution by adding ascorbic acid. Next, the silver recovery is performed by cooling down the solution to a temperature between 5-15°C immediately after the gold recovery. Palladium can be recovered by adding metallic copper powder for chemical cementation. Copper is then recovered by adding tin metal powder for chemical cementation. Finally, zinc metallic powder is added for the recovery of tin.

The leach liquor discharged from the metal extraction process was recycled using a rotavapor to recover HCl for reuse in subsequent batches of the hydrometallurgical process.

The recycling test was performed on a sample with a mixture of the different electronic components ground at 1 cm by using the cutting mill, Retsch SM300. The chemical composition of the mixture has been reported in Table 29.





replications, n.	Au, g/t	Ag, g/t	Pd, g/t	Cu, %	Sn, %
1	253	627	36	18.0	1.89
2	263	597	25	17.3	1.95
3	261	497	23	18.6	2.64
average	253	574	28	17.9	2.16
std dev	16	68	7.0	0.65	0.42

Table 29: Chemical composition of the main elements in the mixture of electroniccomponents; the concentrations are reported as metals.

The concentrations of precious metals in the sample were as follows: Au at 253 g/t, Ag at 574 g/t, and Pd at a low concentration of 28 g/t. The concentration of Cu was 17.9%, and Sn at 2.16%. The operative conditions for the leaching operation were a solid concentration of 15% wt./v, HCl 3.5 mol/L, H_2O_2 (30% wt./v) 20%v/v, $C_2H_4O_2$ (99% wt./v) 10% v/v, time of reaction 3 h and room temperature.

The following is the experimental procedure used for conducting the leaching test by using the prototypal plant; the operations are reported as a function of the time:

- 1. start water loading
- 2. start $C_2H_4O_2$ addition (all the required volume)
- 3. 5 min HCl addition (half of the required volume)
- 4. 10 min H₂O₂ addition (half of the required volume)
- 5. 20 min solid (ground components) loading
- 6. 1 h 25 min HCl addition (25% of all the volume)
- 7. 1 h 30 min H_2O_2 addition (25% of all the volume)
- 8. 2 h 25 min HCl addition (25% of all the volume)
- 9. 2 h 30 min H_2O_2 addition (25% of all the volume)
- 10. 3 h 20 min filtration

In Table 30 the results in terms of the dissolution yields of precious and base metals are reported.

	Au	Ag	Pd	Cu	Sn
concentration, mg/L	36.1	73.4	2.0	24917	2754
dissolution yield, %	95.1	85.3	47.8	92.8	85.0
	รเ	ummary			
	wt. %				
feed	100.0				
solid residue	64.1				

Table 30: Results of the leaching operation for the treatment of the electronic components.

High extraction yields were achieved for the key metal values of interest, with a yield of 95.1% for gold, 85.3% for silver, and 47.8% for palladium. As regards base metals, the dissolution yield was 92.8% for copper and 85.0% for tin. These dissolution efficiency results are significantly higher than those obtained in prior experiments (D5.4 - ANNEX 3) that were conducted on





electronic components without any grinding. The initial grinding step up to 1 cm was crucial to increase the exposure of the metal parts to the leaching solution.

Subsequently the operations to recover the dissolved metals from the leach liquors have been tested according to the outcomes of previous tests. In Table 31 the recoveries for each operation are reported. The results indicate how each element is distributed based on the amount in the leach liquor solution obtained after leaching.

operation	Au, %	Ag, %	Pd, %	Cu, %	Sn, %
Au precipitation	98.5	3.5	2.4	0.0	0.4
Ag precipitation	0.5	85.3	3.1	0.0	0.0
Pd cementation	0.0	0.0	79.5	0.0	0.0
Cu cementation	0.0	10.3	3.7	95.3	0.3
Sn cementation	0.7	0.3	6.1	3.5	89.4
residual solution	0.3	0.6	5.2	1.1	9.9

Table 31: Results of the selective recovery of metals.

Each product obtained was analyzed using ICP-OES after undergoing a chemical attack to determine its specific purity.

The concentration of gold in the final solution was found to be less than 1 mg/L, indicating almost complete precipitation of the metal since 98.5% of recovery has been calculated. The purity of the gold precipitate was determined to be 90.4%. Subsequently, the precipitate was melted in a furnace at 1065°C, and slagging compounds were added to achieve a purity of 99.2%. Additionally, the recovery rates for other metals were measured before and after gold precipitation, and it was determined that only low recoveries of silver, palladium, and tin occurred, but these impurities were almost completely removed during the refining.

Silver recovery was obtained in the form of chloride after cooling the solution at 5°C. The recovery of silver was 85.3% with respect to the initial leach liquor and the purity in AgCl was detected to be 95%. Then, by chemical cementation have been obtained the recoveries of 79.5% of Pd, 95.3% of Cu and 89.4% of Sn. The purities of the final products were 85% for Pd, 92% for Cu, and 96% for Sn.

The prototype plant underwent a successful test, resulting in the adequate extraction of both precious and base metals from the electronic components. Although the purity of the results seems promising, the limited number of electronic components used during the test may have led to experimental errors that could have affected the outcome. Therefore, while the technical feasibility of the hydrometallurgical process Gold-REC 2 has been confirmed, further testing on the pilot plant will be conducted to verify the results, particularly with regard to the purity of the final products. Overall, the testing has demonstrated the effectiveness of the process and the appropriateness of the chosen equipment in the reconfigured hydrometallurgical pilot plant, which could pave the way for a scale-up of the process.

Then, the wastewater generated by the process was characterized by ICP-OES analysis and the composition reported in Table 32 has been determined.





Table 32: Wastewater composition.

Composition of the wastewater generated by Gold-REC 2					
рН	< 1				
HCI	7% wt.				
Zn	34.2 g/L				
Ni	1.48 g/L				
Cu	274 mg/L				
Sn	273 mg/L				
Fe	252 mg/L				
Ti	38 mg/L				
Ag	0.4 mg/L				
Au	0.1 mg/L				
Pd	0.1 mg/L				

Evaporation tests were conducted using a rotary evaporator to obtain a recovery of hydrochloric acid. It is good to keep in mind that hydrochloric acid has an azeotrope so it cannot be recovered to a purity greater than 20% wt./v. In Figure 27 a picture of the adopted equipment has been showed.



Figure 27. Rotary evaporator used for tests on HCl recovery.

Tests were conducted at 60°C by vacuum working at 0.3 bar according to the scheme shown in Figure 28.



Figure 28. Flowsheet of the HCl evaporation process.





Evaporation was then carried out in series 3 times, and then three HCl solutions were obtained with decreasing concentrations and a sludge rich in zinc chloride that must be properly disposed of. The timing was one hour for the first two stages and two hours for the third. Table 33 presents the material balance for the various streams depicted in the preceding process flowsheet. It provides information about the input of one ton of wastewater and the four corresponding outputs.

input/output	S101	S102	S105	S106	S107
total mass, kg	1000	304.2	136.3	390.4	169.1
HCl, kg	70.0	45.5	15.6	3.9	0.0
H ₂ O, kg	857.5	258.8	120.7	386.5	96.6
ZnCl ₂ , kg	69.2	0.0	0.0	0.0	69.2
NiCl ₂ , kg	3.3	0.0	0.0	0.0	3.3

Table 33: Mass balance of the HCl evaporation process.

By assuming one ton of wastewater with a concentration of 7% wt. HCl, the hydrochloric acid can be recovered using a 3-stage process in series, with a recovery rate of nearly 100%. The first step results in a solution containing 14.9% wt. HCl, the second step produces a solution containing 11.4% wt. HCl and the third step produces a solution containing 1.0% wt. HCl. By combining the first two outputs (S102 and S105), a solution with an HCl concentration of around 13.8% wt. can be obtained, which can be recycled back into the leaching solution used for the Gold-REC 2 recycling process. The leaching solution requires a 3 mol/L HCl, which corresponds to about 11% by weight. The mass recovery of the solution with 13.8% wt. of HCl is about 44% by weight with respect to the initial wastewater (S101) and can be reused in the process itself. The remaining sludge, which accounts for approximately 17% of the weight of the wastewater feed, mainly consists of zinc and nickel chloride and must be disposed of properly.





2.2.2 Process analysis

This section outlines the process flowsheet that was developed during experimental activities, based also on the results obtained at the pilot scale. The process enables the recovery of precious metals (such as Au, Ag, and Pd) and base metals (like Cu and Sn) from the PCBs of critical car components (combimeter, infotainment system, rain sensor, brake lights, etc..). Specifically, the process was tested on different car models, including defective parts from SEAT and materials from dismantlers such as ILSSA and POLLINI collected from End-of-Life Vehicles (ELVs). The tests were performed on the PCBs of the combimeter, but this optimized hydrometallurgical recycling process can be easily replicated on PCBs from other critical car components.

To maximize the dissolution yields of the metals of interest, a preliminary disassembly phase is necessary. Certain electronic components must be removed as they may inhibit dissolving yields or increase reagent consumption due to their chemical composition. These components are electromagnets, transducers, aluminum capacitors, and crystal oscillators; and their weight compared to the whole PCB is generally around 10-15%. Essentially, in the hydrometallurgical process, a high copper content in the solid would increase the acid consumption to dissolve the copper and ensure the subsequent recovery of the precious metals. Thus, it also adversely affects operating costs and environmental impact. This is the case for components such as electromagnets that have a copper coil. In addition, the presence of steel and aluminum negatively affects the dissolution of metals as they are reducing agents; this is the case for capacitors and transducers. These kinds of components are not suitable for hydrometallurgical treatments, but some metals could probably be recycled by heat treatment.

In addition, it was deducted that is recommended to remove components that contain high amounts of gold and have gold on their surface, such as connectors with gold pins, golden wires, and small PCBs with gold contacts. This will maximize the recovery yields as a specific hydrometallurgical treatment has been identified for these gold-plated components. Generally, the percentage by weight of these components is around 5% depending on the type of PCB. After carrying out a preliminary crushing operation to obtain a particle size of 1 cm, the recovery of precious and base metals from these components can be done through the hydrometallurgical process that has been validated within the project resulting from the Gold-REC 2 patent.

As shown in Figure 17, the dismantling of electronic components can be accomplished while reducing manual labour for operators using COBOT technology. This method has been thoroughly tested by POLIMI and the results are documented in D6.1.

After removing the components from the electronic board, the remaining board with some residual components is cut down to a particle size of less than 2mm using a cutting mill. Generally, this fraction is about 80% by weight of the whole PCB. The resulting PCB powder contains precious and base metals that can be extracted using the validated hydrometallurgical process. This process is based on the Gold-REC 1 patent and has been tested on a pilot scale to ensure its efficiency.





2.2.2.1 Process analysis – Gold-REC 1

This section describes the results obtained, the mass and energy balances, and a preliminary economic analysis to assess the economic feasibility of the optimized Gold-REC 1 process for the treatment of PCB powders. The results for most of the process operations derive from pilot scale tests in terms of extraction yields and purity achieved. As regards the initial chemical composition, the SEAT IBIZA IV composition was taken into account, since the material provided by ILSSA on which the pilot tests were conducted had a significantly lower content for all metal values. Obviously, the sustainability of this process is strongly dependent on the content of the main metal values such as gold and copper; therefore, for the execution of the hydrometallurgical process, it is fundamental to carry out chemical analyses to evaluate the quality of the material to be processed.

Figure 29 shows the flowsheet of the process that has been optimized within the TREASURE EU project activities and tested on a pilot scale. This process is derived from the Gold-REC 1 patent [9].



Figure 29. Flowsheet of the Gold-REC 1 process for the recycling of powders of PCBs.

As mentioned before, to proceed with this process, it is necessary to disassemble some electronic components from PCBs (as shown in Figure 18). After that, the material needs to be ground to a particle size of 2 mm. This is important as it increases the specific surface area and exposure of the material to acids.

The hydrometallurgical process has two stages- base metal dissolution and precious metal dissolution (gold and silver). The performance of the first stage affects the efficiency of the second stage. The first stage has three counter-current leaching steps using sulfuric acid (1.8 mol/L) and hydrogen peroxide at 30% wt. (5-10% v/v). In the first and second steps, 5% v/v hydrogen peroxide is added, while in the third step, 1.8 mol/L sulphuric acid and 10% v/v hydrogen peroxide are added. From the solution in which the base metals have been dissolved, metastannic acid is first recovered by precipitation by the addition of 2.5 mL/L polyamine 10%





w/v which is then subjected to a thermal treatment (650 °C per 1 hour) to obtain tin oxide. Then the residual solution is sent to the recovery of the metallic copper by electrodeposition. Instead, the solution in which precious metals have been dissolved is sent to electrodeposition, which simultaneously recovers gold and silver. The recovered product is called dorè, which is then refined to selectively extract silver and gold. For this purpose, a nitric acid leaching solution (1 mol/L) is used to dissolve the silver in the form of nitrate. The final product is a solid with a high purity of gold, that is further refined by a thermal treatment at 1065°C. The silver is also recovered from the solution in which it was dissolved, by adding sodium chloride (40 g/L) to form silver chloride.

The two solutions generated during the process, wastewater1 and wastewater2, can be recycled up to 80% in the preparation of the leaching solutions for dissolving base and precious metals. This recycling significantly reduces the amount of freshwater used during the process and consequently, minimizes the amount of wastewater generated, following the MLD approach. The reason for this recycling is that the process of electrodeposition allows partial regeneration of some reagents, such as increasing free acidity and partially regenerating thiourea. Specifically, after electrodeposition wastewater1 has a sulfuric acid concentration of 1.51 mol/L, while wastewater2 has a thiourea concentration of about 18 g/L. Therefore, this approach also results in considerable savings in the reagents needed for the leaching operations.

In addition, to further increase the environmental sustainability of the process from a water use perspective, two specific sections have been defined for the treatment of the remaining 20% of the two wastewaters. These sections allow the obtaining of treated water with quality characteristics such as to be used for other purposes as service water. Figure 30 shows the two sections for the wastewater treatment.



b)

Figure 30. Wastewater treatment sections. a) wastewater 1; b) wastewater 2.





The section shown in Figure 30 a) is the wastewater treatment section from which base metals are recovered. This section consists of a first operation aimed at further recovery of copper from the solution by chemical cementation with the addition of metallic iron and a second operation of pH correction with the addition of lime that allows the transfer of pollutants in the form of a sludge consisting predominantly of calcium sulphate and the obtaining of treated water with characteristics suitable for discharge into the sewer or for reuse in the plant as service water.

The section displayed in Figure 30 b) is specifically designed for treating the wastewater generated by the leaching stage, which is used for recovering precious metals. Thiourea, an organic acid, is used in the process, which results in the presence of COD in the solution. Therefore, a Fenton treatment is employed to break down the organic substances into simpler and easily biodegradable substances. As the solution already contains a moderate amount of iron, the use of ferrous sulphate, one of the Fenton reagents, along with hydrogen peroxide, is limited. Next, lime is added to raise the pH to 8, which causes the precipitation of pollutants into sludge, mainly composed of calcium sulfate and ferric hydroxide. The resulting water is of good quality and can be discharged as sewage or used as service water in the plant. Specifically, treated water can be reused in the process as washing water to clean the final products and the solid residues.

The process analysis was referred to the PCBs of the SEAT IBIZA IV combimeter. The powders to be subjected to the hydrometallurgical process Gold-REC 1 constitute 78.44% of the weight of the PCB. Table 34 shows the chemical composition of metals recovered through this process. Although it is possible to recover palladium by an additional hydrometallurgical treatment on the solid residue of the process, its content is very low, and the recovery efficiency would not be satisfactory.

	Au, g/t	Ag, g/t	Pd, g/t	Cu, %	Sn, %
average	94.2	273.3	27.5	19.1	1.01
std dev	27.6	129.4	3.3	2.69	0.24

Table 34: Chemical composition of PCBs powders (SEAT IBIZA IV).

Table 35 shows the results obtained in terms of dissolution efficiencies and selective recovery of different metals from solutions, allowing us to determine each metal's overall recovery.

atora	Recovery					
stage	Au	Ag	Cu	Sn		
1 st leaching stage			99.2%	97.2%		
2 nd leaching stage	80.5%	89.1%				
Sn precipitation				94.2%		
Cu electrowinning			98.1%			
Au – electrodeposition + refining	98.0%					
Ag – electrodeposition + refining		76.0%				
overall	78.9%	67.7%	97.3%	91.6%		

Table 35: Gold-REC 1 hydrometallurgical process efficiencies in terms of metals recovery based on the results obtained at pilot scale.





This hydrometallurgical process was tested on PCB powders from different car models at a pilot scale. The process resulted in metal recoveries of 78.5% Au, 67.7% Ag, 97.3% Cu, and 91.6% Sn.

Table 36 outlines a comprehensive mass balance that considers all the inputs and outputs of the hydrometallurgical process and wastewater treatment sections. This mass balance has been formulated based on the outcomes of the pilot tests, and it pertains to the treatment of 1 ton of PCBs.

Input	kg	Output	kg		
Solid	1000.0	Dry solid residue	781.0		
H ₂ SO ₄ (50 % w/v)	767.1	Treated water 1	2194.8		
H ₂ O ₂ (30 % w/v)	1771.2	Treated water 2	1736.4		
Thiourea	40.7	Wet sludge 1	255.7		
Ferric sulphate	181.9	Wet sludge 2	364.1		
Polyamine (10 % w/v)	19.1	Tin oxide	11.85		
Water for 1 st leaching stage	281.5	Copper 1	187.0		
Water for 2 nd leaching stage	1390.1	Gold	0.075		
Water for Au-Ag refining	2.4	Silver chloride	0.245		
Iron metallic powder	0.7	Humidity	755.3		
HNO₃ (65 % w/v)	0.2	Copper 2 from the WW section	0.7		
NaCl	0.1	Wastewater from the refining	2.7		
Lime (10% w/v)	1054.3				
Ferrous sulphate	13.2				
Total input	6522.5	Total output	6289.9		
Experimental error 3.6%					

Table 36: Mass balance for the treatment of 1 ton PCBs powder by adopting Gold-REC 1 process at pilot scale.

It's worth noting that by reusing solutions, freshwater consumption can be decreased by over 85% (1674 kg of this scenario compared to 12045 kg of the previous scenario reported in D5.4 -ANNEX 3). Another important benefit of this process is that it doesn't generate wastewater, as it is sent to specific sections and purified for reuse within the plant. The only wastewater generated is from gold and silver refining treatment, but this amount is very low - only 2.7 kg per ton of processed PCB powders.

This process allows the recovery of 0.075 kg of gold, 0.245 kg of silver chloride, 11.85 kg of tin oxide, and about 187 kg of copper from treating one ton of PCB powders. The purity of the obtained products is shown in the next tables. All other outputs, including their characterization, are given below.

Table 37 clearly presents the purity levels of high-value products that can generate substantial revenue. Quantities based on 1 ton of processed PCB powders, their form, and impurities are reported.





Table 37: Mass and purity of the various products obtained by the Gold-REC 1 process for recycling 1 ton of PCB powders validated at pilot scale.

	gold	silver	tin	copper 1	copper 2
mass	75 g	245 g	11.85 kg	187.0 kg	0.7 kg
form	metal	chloride	oxide	metal	metal
purity, wt. %	99.1	99.8	99.1	99.4	97.2
impurities, wt. %	Cu 0.7 sulphates 0.2	nitrates 0.2%	CuO 0.6 polyamine 0.1	Fe 0.3 Ni 0.2 Zn 0.1	Fe 2.8

About the other outputs, "dry solid residue" refers to the remaining powder of PCBs that is obtained after the leaching process to dissolve base and precious metals. From one ton of processed PCB powders, the amount of dry solid residue is 781 kg. The dry solid is composed of mainly plastics and fiberglass beyond a residual metal fraction detected by a chemical attack that is about 3-4% wt. The residual metal contents have been reported in Table 38.

Dry solid residue metal characterization				
Al, wt. %	2.85			
Ti, wt. %	0.23			
Fe, wt. %	0.15			
Cu, wt. %	0.12			
Ni, g/t	757			
Zn, g/t	451			
Sn, g/t	336			
Zr, g/t	71.1			
Ag, g/t	33.9			
Pd, g/t	33.1			
Au, g/t	23.5			

Table 38: Dry solid residue metal characterization.

It can be observed that the solid residue mainly consists of 2.85% aluminum, 0.23% titanium, 0.15% iron, and 0.12% copper. Additionally, it's important to note that almost all the initial palladium is present in the solid residue. Therefore, if the solid residue has a higher concentration of palladium, it can be used for the recovery of palladium through another hydrometallurgical treatment.

Then, "humidity" refers to the water that remains on the solid after separating the leach liquor solution from the solid and to the water associated with the products.

In Table 39, the outputs of the wastewater sections are reported in terms of treated water and wet sludge.





Table 39: Wastewater sections outputs.

Treated water 1	Treated water 2	Wet sludge 1	Wet sludge 2
pH: 8 Cu, Al, Ni, Fe, Sn, Zn, Ti < 2 mg/L traces of calcium hydroxide	pH: 8 COD: 375 mg/L Cu, Al, Ni, Fe, Sn, Ti, Ag < 2 mg/L	calcium sulphates iron hydroxides aluminum hydroxides nichel hydroxides	calcium sulphates copper hydroxides aluminum hydroxides

The water that is produced has quality characteristics that make it suitable for either drainage into sewage or for reuse as service water within the plant. It is particularly useful for the recycling process, such as washing water to clean solids and final products. Regarding the sludges, they must be disposed of properly.

Another important output to safely dispose of is the wastewater produced during the selective recovery of silver from gold, even though the volume generated is minimal. This wastewater mostly comprises nitric acid with a concentration of approximately 0.3 mol/L and contains a significant amount of sodium nitrate.

Based on the material balance determined through tests conducted on a pilot scale for almost all process operations, it was possible to evaluate the economic feasibility of the process. Table 40 reports the OPEX by considering quantities of chemicals used to treat 1 ton of PCB powders, disposal costs for residual solids and solutions and energy consumptions.

Chemical	Amount, kg	Cost per unit, €/kg	Cost, €
H ₂ SO ₄ (50 % w/v)	767.1	0.13	99.7
H ₂ O ₂ (30 % w/v)	1771.2	0.35	619.9
HNO₃ (65 % w/v)	0.2	0.20	0.04
Thiourea	40.7	1.0	40.7
Ferric sulphate	181.9	0.30	54.6
Polyamine (10 % w/v)	19.1	1.0	19.1
Iron metallic powder	0.7	1.2	0.8
NaCl	0.1	0.12	0.012
Lime (10% w/v)	1054.3	0.015	15.8
Ferrous sulphate	13.2	0.10	1.3
Water	1674.0	0.0015	2.5
			854.5€
Output	Amount, kg	Cost per unit, €/kg	Cost, €
Dry solid residue	781.0	0.6	468.6
Treated water 1	2194.8	0.0005	1.1
Treated water 2	1736.4	0.0005	0.9
Wet sludge 1	255.7	0.15	38.4

Table 40: Chemical consumptions and costs for the treatment of 1 ton of PCBs powders.





Wet sludge 2	364.1	0.15	54.6
Wastewater from the refining	2.7	0.20	0.5
			564.1€
Operation	Energy consumption, kWh	Cost per unit, €/kWh	Cost, €
Stirring	29	0.40	11.6
Pumps	35	0.40	14.0
Furnace for tin refining	123	0.40	49.2
Cu electrodeposition (2.3 kWh/kg)	430	0.40	172.0
Au-Ag electrodeposition (13.0 kWh/kg)	3.5	0.40	1.4
Furnace for Au refining	6.0	0.40	2.4
Wastewater section	15	0.40	6.0
			256.6€
	1675.2€		

The total cost of chemicals is $854.5 \in$, which has been reduced by almost 30% thanks to the recirculation of the solutions. Hydrogen peroxide contributes the most, accounting for about 72% of the total cost of chemicals.

The total cost of managing the solid waste and the solutions generated by the process is $564.1 \in$. The cost of energy consumption is $256.6 \in$, which was estimated based on pilot scale tests for treating 1 ton of PCB powders. The energy consumptions taken into account include stirring for leaching operations, pumps for discharging solutions from chemical reactors and electrolytic cells, furnaces for refining tin oxide and gold, and those for electrodepositions. In this analysis, we did not take into account the costs of operators, which are clearly influenced by the plant size, level of automation, and the location of the hydrometallurgical plant.

Regarding the revenues, they are mainly dependent on the economic value of gold, which is currently growing strongly. For this reason, the economic value of gold considered for revenue estimation was the average economic value over the last 5 years, according to Figure 31.

Gold Prices - Historical Annual Data							
Year	Average Closing Price	Year Open	Year High	Year Low	Year Close	Annual % Change	
2024	\$2,159.47	\$2,064.61	\$2,386.60	\$1,992.06	\$2,338.59	13.36%	
2023	\$1,943.00	\$1,824.16	\$2,115.10	\$1,811.27	\$2,062.92	13.08%	
2022	\$1,801.87	\$1,800.10	\$2,043.30	\$1,626.65	\$1,824.32	-0.23%	
2021	\$1,798.89	\$1,946.60	\$1,954.40	\$1,678.00	\$1,828.60	-3.51%	
2020	\$1,773.73	\$1,520.55	\$2,058.40	\$1,472.35	\$1,895.10	24.43%	

Figure 31. Gold prices (\$/ounce) in the last five years. Source: Macrotrends [10].

Therefore, based on these data, the average gold price in the last five years is 1750.6 \$/ounce which corresponds to 62.15 €/g. In addition, the economic value takes into account the form in which the specific element is recovered and its purity. Thus, the economic value is depreciated





by a percentage equal to the purity obtained in the final products. To be even more realistic, an additional scenario has been added. In this scenario, due to the products not having a purity of 100%, there is a further depreciation of 10%.

Based on these considerations, Table 41 reports the OPEX and revenues for the treatment of 1 ton of PCB powders. As regards revenues, as explained above, two scenarios were considered: the first one, called revenue A, taking into account the purity and form of the product obtained, and the second one, called revenue B, where there is also a further depreciation of 20%.

Item	Cost, €	Revenue A, €	Revenue B, €
Grinding of PCBs (750 kWh)	300.0		
Chemicals	854.5		
Energy consumption	256.6		
Solid and residual solution management	564.1		
Gold (purity 99.1%), value 61.6 €/g		4619.5	3695.6
Silver chloride (purity 99.8%) value 471.9 €/kg		115.6	92.5
Copper 1 (purity 99.4%) value 8.24 €/kg		1540.6	1232.5
Copper 2 (purity 97.2%) value 8.06 €/kg		5.6	4.5
Tin oxide (purity 99.1%) value 15.76 €/kg		186.7	149.3
profit per ton of PCBs powders		+ 4492.9 €	+3199.3€

Table 41: OPEX and revenues for the treatment of 1 ton of PCBs powders.

Thus, this process is also significantly feasible from an economic point of view since each ton of processed material can generate a high profit, in the range of $3199.3 \in -4492.9 \in$ based on the agreements that could be made for the sale of recovered products.

It remains outside this preliminary economic analysis the operator effort required for the first level of disassembly, which involves recovering PCBs from critical car components like the combi meter. The second disassembly level instead involves removing specific electronic components from the board, which could be performed using a COBOT (more explanations are given in D6.1). Additionally, agreements need to be made for the purchase of PCBs by the recycler who plans to build the plant and process this material.

2.2.2.2 Process analysis - Gold-REC 2

This section describes the results obtained, the mass and energy balances, and a preliminary economic analysis to assess the economic feasibility of the optimized Gold-REC 2 process for the treatment of gold-plated electronic components. The results for most of the process operations derive from the prototypal plant in terms of extraction yields and purity achieved.

As for the initial chemical composition, we consider a mixture of electronic components from the combi meter of various PCBs, such as FIAT and SEAT, as the material has been supplied by POLLINI and SEAT.

Figure 32 shows the flowsheet of the process that has been optimized within the TREASURE EU project activities and tested on a pilot scale. This process is derived from the Gold-REC 2 patent [11]. A section was also implemented for the recovery, by evaporation, of hydrochloric acid from the solution used to selectively recover different metals. This process allows for the reuse of





hydrochloric acid in preparing the leaching solution, reducing its consumption and simplifying wastewater management. The only outputs that require expensive disposal now are the solid leaching residue and the residual evaporative sludge concentrate containing zinc chloride.



Figure 32. Gold-REC 2 hydrometallurgical process flowsheet for the treatment of electronic components of PCBs.

The process for treating gold-plated electronic components of PCBs (as shown in Figure 18) allows for the recovery of gold, silver in the form of chloride, palladium, copper, and tin through a series of hydrometallurgical treatments. Generally, these fractions correspond to 5% by weight of all the PCB.

The process involves leaching both base and precious metals using a leaching system with the following reagents: HCl 3.5 mol/L, $C_2H_4O_2$ (99%) 10% v/v, H_2O_2 (30% w/v) 20% v/v. After dissolving the metals, a series of operations are performed to selectively recover them. Adding 5 g/L ascorbic acid allows for the recovery of gold ascorbate, which is then thermally refined for high-purity gold production. Cooling the solution to 5°C precipitates silver as silver chloride due





to its low solubility at low temperatures. Palladium, copper, and tin are recovered through chemical cementation by adding copper, tin, and zinc metal powders, respectively. It's important to accurately define the dosage of these metal powders to maintain product purity. For example, the copper dosage for palladium recovery was 6 g/L, tin for copper recovery was 28 g/L (60% compared to stoichiometric conditions), and the zinc powder dosage for tin recovery was 1 g/L (70% compared to stoichiometric conditions). The dosages for chemical cementation depend on the chemical composition of the processed electronic components.

The solution containing the metals is sent to a rotary evaporator to recover hydrochloric acid for reuse in the recycling process. Three consecutive stages of operation have been studied to obtain the first two condensates, which together have a concentration of hydrochloric acid of almost 14% by weight. The third step produces a liquid stream with a concentration of 1% HCl by weight that can still be reused in the plant for specific applications or for washing. Finally, zinc and nickel chloride concentrate is produced and must be disposed of appropriately.

The process analysis referred to a mixture of electronic components such as connectors of different sizes, golden wires, and small PCBs (supplied by SEAT and POLLINI). The fraction corresponds to the 4.4% by weight of a combi meter PCB. Table 42 shows the chemical composition of the mixture.

	Au, g/t	Ag, g/t	Pd, g/t	Cu, %	Sn, %
average	253	574	28	17.9	2.16
std dev	16	68	7.0	0.65	0.42

Table 42: Chemical composition of the main elements in the mixture of electronic components.

Table 43 shows the results obtained in terms of dissolution efficiencies and selective recovery of different metals from the solution, which then allowed us to determine the overall recovery of each metal.

Table 43: Gold-REC 2 hydrometallurgical process efficiencies in terms of metals recovery based on the results obtained by the prototypal plant.

stago			Recovery %		
Stage	Au	Ag	Pd	Cu	Sn
Leaching stage	95.1	85.3	47.8	92.8	85.0
Au recovery	98.5	3.5	2.4	0.0	0.4
Ag recovery	0.5	85.3	3.1	0.0	0.0
Pd recovery	0.0	0.0	79.5	0.0	0.0
Cu recovery	0.0	10.3	3.7	95.3	0.3
Sn recovery	0.7	0.3	6.1	3.5	89.4
Residual solution	0.3	0.6	5.2	1.1	9.9
overall	93.7	72.8	38.0	88.4	76.0





The process resulted in metal recoveries of 93.7% Au, 72.8% Ag, 38.0% Pd, 88.4% Cu and 76.0% Sn. The recovery rates achieved are remarkably satisfactory, except for palladium. A low dissolution of palladium was observed during leaching of about 48%; this may be due to the fact that the content of palladium in the initial material is very low (28 g/t), which could influence its efficiency. In fact, hydrometallurgical processes for the treatment of PCBs, given their high heterogeneity, have a certain limit in recovering metals from the solid, always remaining a certain amount that they are not able to bring into solution.

Table 44 outlines a comprehensive mass balance that considers all the inputs and outputs of the hydrometallurgical process and hydrochloric acid recovery section. This mass balance has been formulated based on the outcomes of the prototypal tests for the hydrometallurgical section and based on the lab-test for the evaporation section.

Input	kg	Output	kg		
Solid	1000.0	Dry solid residue	641.0		
HCl (32 % w/v)	1257.1	Gold	0.239		
H ₂ O ₂ (30 % w/v)	1480.0	Silver chloride	0.584		
C ₂ H ₄ O ₂ (80% w/v)	890.8	Palladium	0.0125		
Water	390.6	Copper	172.1		
Ascorbic acid	33.3	Tin	17.1		
Copper metallic powder	40.0	HCl (1% w/v)	2857.0		
Tin metallic powder	186.7	Sludge	1237.0		
Zinc metallic powder	6.7	Humidity	185.2		
Total input	5285.1	Total output	5110.2		
Experimental error 3.3%					

Table 44: Mass balance for the treatment of 1 ton of electronic components by the Gold-REC2 process based on the results of the prototypal plant.

The introduction of the evaporation section has made it possible to reduce the consumption of freshwater by allowing the reuse of the solutions. In fact, the consumption of fresh water is only 390.6 kg per ton of electronic components to be treated. For every ton of processed material, the following products are obtained: 239 g of gold, 584 g of silver chloride, 12.5 g of palladium, 172 kg of copper, and 17 kg of tin.

Below are the outputs of the process obtained with the aim of highlighting mainly the purity of the products obtained and the chemical composition of the other outputs to define proper management.

Firstly, Table 45 shows the purity of the obtained products, their form, and the main detected impurities. Analyses have been performed by ICP-OES analysis after specific chemical attacks. Reported quantities referred to 1 ton of processed electronic components.





	gold	silver	palladium	copper	tin
mass	239 g	584 g	12.5 g	172.1 kg	17.1 kg
form	metal	chloride	metal	metal	metal
purity, wt. %	99.2	95.0	84.9	92.3	96.1
impurities	Ag	Zn, Pd	Cu	Sn	Zn, Fe, Ni

Table 45: Mass and purity of the various products obtained by the Gold-REC 2 process forrecycling 1 ton of electronic components validated by the prototypal plant.

The purity of the products obtained was as follows: 99.2% for gold, 95.0% for silver chloride, 84.9% for palladium, 92.3% for copper, and 96.1% for tin. The impurities were determined qualitatively since the quantities obtained from the final products were very low. This was due to the fact that only a limited number of electronic components were supplied by the industrial partners of the project. The presence of silver traces in gold may be due to its lower melting temperature compared to gold, causing a slight impurity to remain during thermal refining at 1065°C. Other impurities are primarily a result of the metal being treated for chemical cementation and the presence of other metals in the leaching solution.

Regarding the other outputs, "dry solid residue" refers to the leaching solid residue of electronic components. From one ton, 641 kg of this fraction is obtained. The dry solid is composed of mainly plastics, and then also from fiberglass. The undissolved metal fraction due to the very strong leaching solution is very low, around 2-3% by weight, although many trace metals are determined. The residual metal contents have been reported in Table 46.

Dry solid residue metal characterization			
Cu, wt. %	2.18		
Sn, wt. %	0.51		
Ni, wt. %	0.31		
Ti, g/t	785		
Zn, g/t	162		
Ag, g/t	132		
Fe, g/t	39.7		
Pd, g/t	22.8		
Au, g/t	19.3		
Pb, g/t	17.9		

Table 46: Dry solid residue of Gold-REC 2 process characterization.

It is evident from the table that the solid residue primarily contains 2.18% copper, 0.51% tin, 0.31% nickel, and trace amounts of other metals.

The output "humidity" refers to the water that remains on the solid after separating the leach liquor solution from the solid and to the water associated with the products.

The other outputs, "HCl 1% wt." and "sludge," are produced during the evaporation process. They are obtained from the third step of evaporation. HCl 1% wt. is a solution that can be reused





in the industrial plant for various applications, while the sludge is a concentrate of salts, such as 40.9% zinc chloride and 1.9% nickel chloride.

Based on the material balance determined through tests conducted on the prototype plant, it was possible to evaluate the economic feasibility of the process. Table 47 reports the operating expenses (OPEX) by considering the quantities of chemicals used to treat 1 ton of electronic components, disposal costs for residual solids and solutions, and energy consumption.

Chemical	Amount, kg	Cost per unit, €/kg	Cost, €
HCl (32 % w/v)	1257.1	0.17	213.7
H ₂ O ₂ (30 % w/v)	1480.0	0.35	518.0
C ₂ H ₄ O ₂ (80% w/v)	890.8	0.35	311.8
Ascorbic acid	33.3	2.5	83.3
Copper metallic powder	40.0	1.2	48.0
Tin metallic powder	186.7	1.5	280.0
Zinc metallic powder	6.7	2.0	13.3
Water	390.6	0.0015	0.6
Steam	7489.3	0.083	621.6
	-		2090.3€
Output	Amount, kg	Cost per unit, €/kg	Cost, €
Dry solid residue	641.0	0.6	384.6
HCl, 1% wt. solution	2857.0	0.0	0.0

Table 47: Chemical consumption and costs for the treatment of 1 ton of electronic components.

			632.0€
Operation	Energy consumption, kWh	Cost per unit, €/kWh	Cost, €
Stirring	18	0.40	7.2
Pumps	32	0.40	12.8
Furnace for Au refining	6.0	0.40	2.4
Recirculation pump for evaporation	227	0.40	90.9
			113.3€
OPEX			2835.6€

1237.0

0.2

247.4

The total cost of chemicals, including the cost of steam for evaporation, amounts to ≤ 2090.3 . Among the chemical reagents, hydrogen peroxide has the greatest impact. However, steam has an even greater effect on the total cost. The benefits are evident since through evaporation, it is possible to recover hydrochloric acid and then halve its total consumption.



Sludge



The total cost of managing solid waste is 632.0€. The condensate obtained from the third stage of evaporation is a clean solution of HCl at 1 wt. % and has not been considered as either a cost or revenue. It can be used in the plant as a service solution.

The cost of energy consumption is 113.3€, which was estimated based on tests conducted on the prototype plant for treating 1 ton of electronic components. This cost covers the energy consumption for stirring, pumps used to transfer or recirculate the solutions, and the furnace for gold refining. The total OPEX is 2835.6€ per ton of processed material. It's important to note that this analysis does not consider the costs of operators, which are influenced by factors such as the plant size, level of automation, and the location of the hydrometallurgical plant.

The revenues are heavily dependent on the economic value of gold, which is currently experiencing strong growth. Therefore, the revenue estimation considers the average economic value of gold over the last 5 years, as illustrated in Figure 31 in the previous paragraph. The economic value of the other elements was determined based on their form (whether they are recovered as metals or salts) and the purity obtained. The economic value was adjusted based on the percentage of purity. To be more realistic, an alternative scenario was presented, considering a further 20% depreciation of the products obtained. The actual sales value of the products can only be defined once agreements are made with interested customers.

Based on these considerations, Table 48 reports the OPEX and revenues for the treatment of 1 ton of electronic components. As regards revenues, as explained above, two scenarios were considered: the first one, called revenue A, considering the purity and form of the product obtained, and the second one, called revenue B, where there is also a further depreciation of 20%.

Item	Cost, €	Revenue A, €	Revenue B, €
Crushing of electronic components (500 kWh)	200.0		
Chemicals	2090.3		
Energy consumption in the recycling process	113.3		
Solid waste management	632.0		
Gold (purity 99.2%), value 61.66 €/g		14730	11784
Silver chloride (purity 95.0%) value 449.2 €/kg		262.4	209.9
Palladium (purity 84.9%) value 24.3 €/g		304.5	243.6
Copper (purity 92.3%) value 7.6 €/kg		1312.3	1049.9
Tin (purity 96.1%) value 29.3 €/kg		500.6	400.5
profit per ton of PCBs powders		+ 14074.4 €	+10652.4 €

Table 48: OPEX and revenues for the treatment of 1 ton of electronic components from PCB.

The hydrometallurgical process is highly environmentally sustainable due to its low water consumption and hydrochloric acid recovery from generated wastewater. It is also significantly sustainable from an economic standpoint, as each ton of processed material can generate a high profit, ranging from 14074€ to 10650€ based on potential agreements for the sale of recovered products.

The technical and economic feasibility of implementing this process in an industrial plant remains a challenge due to the difficulty of collecting large quantities of electronic components from the automotive sector. The electronic components suitable for the Gold-REC 2 process



65



make up 4.4% of the weight of the combineter PCBs. Expanding the discussion to include PCBs from other critical car components would increase the number of electronic components obtained from a car. However, the labor-intensive disassembly process and the large number of machines needed to obtain sufficient quantities for developing an industrial plant still present significant challenge. To mitigate this issue, these electronic components could potentially be processed in the same plant alongside other materials with similar characteristics.

2.2.3 Discussion

The hydrometallurgical process for recycling precious metals (Au, Ag, and Pd) and base metals (Cu and Sn) from PCBs obtained from car combimeters has been successfully tested at a pilot scale. Prior to the start of the EU Treasure project, UNIVAQ already held patents for the processing of PCBs, known as Gold-REC 1 [9] and Gold-REC 2 [11].

As part of the project, the recycling process was extensively studied through laboratory and pilot-scale experiments. The process was optimized using combimeter PCBs provided by project partners such as SEAT, POLLINI, and ILSSA. The decision to use combimeters was a common choice for the project, based on a priority ranking of critical car parts, considering factors such as thermodynamic rarity and disassembly time, provided to the project by UNIZAR's activities. Compared to the patents, UNIVAQ has optimized the recycling process within the project to maximize yields, reduce the consumption of reagents and freshwater, and minimize the production of wastewater. The goal was to obtain an economically feasible process developed using an MLD approach.

The main innovations achieved thanks to the activities carried out in the project are listed below:

- Certain specific electronic components on the PCB have been identified for preliminary removal. These components include electronic components that inhibit metal dissolution yields in the process, as well as gold-plated electronic components that are better suited for a separate hydrometallurgical process. More details are available in section 2.2.1.
- UNIVAQ transferred the information of the components to be removed to POLIMI, which could then test the removal of these specific electronic components using COBOT technology. This reduced manual work for the disassembly operation.
- After completing the disassembly operation, two hydrometallurgical processes were identified. The first process is for treating the board with residual electronic components, using hydrometallurgical technology optimized from the Gold-REC1 patent. The second process is for treating gold-plated electronic components, optimized based on the patented technology of the Gold-REC 2 process.
- The benefits of disassembly are evident in terms of increased dissolution yields. In particular, the Gold-REC1 process, after disassembly, allows for the dissolution of 80.5% of the gold, compared to 45.3% obtained if some electronic components were not removed. Reference has been made to gold as it is the main intrinsic economic value of the PCB.
- In the Gold-REC 1 process, the dissolution stage of base metals has been optimized through factorial experimentation that allowed a more intelligent use of hydrogen peroxide. An additional step has been introduced but with a lower overall amount of hydrogen peroxide consumed. These adjustments have allowed for higher yields in the dissolution of the metals of interest.
- During the Gold-REC 1 process, a partial regeneration of reagents such as sulfuric acid and thiourea was observed after the electrodeposition operation. This has enabled a





recycling rate of 80% for the solutions, reducing overall reagent consumption. Additionally, two wastewater treatment sections have been incorporated into the recycling process to manage the remaining 20% of wastewater. This results in a process that does not generate contaminated wastewater, thus avoiding high disposal costs.

- The Gold-REC 2 process now includes a preliminary crushing step of up to 1 cm, allowing for better exposure of metals to acids and increased dissolution yields. Furthermore, in addition to optimizing reagent dosages, a final section has been added for the recovery of hydrochloric acid from process wastewater through evaporation. This has led to reduced consumption of freshwater and reagents.
- The Gold-REC 1 process underwent pilot-scale testing, while the Gold-REC 2 process was tested using a prototype plant. ILSSA personnel received training as potential end-users of the technology developed within the project.

Results have confirmed that, once the PCB is obtained, the implemented processes can generate a profit and allow to minimize the production of wastewater compared to the UNIVAQ patents.

Currently, the limits for the development of this process at the industrial level are the following:

- The disassembly stage involves removing the PCB from the individual critical car components. Despite UNIZAR having defined the procedures for disassembly and the necessary tools, this phase requires time, which could unavoidably increase in the case of crashed cars.
- The high variability in the chemical composition, especially in the gold content, of PCBs in critical components depends on the different car models. This variability is a critical aspect of the process as it directly influences the economic feasibility of the recycling process. This issue could be solved by establishing the traceability of the electronic components and knowing the chemical composition in advance; UNIVAQ has provided its contribution to the CEN Workshop Agreement developed by UNI in cooperation with most of the partners.

To assess the viability of investing in the construction of an industrial plant for the recycling of PCBs, a preliminary analysis was conducted to understand the availability of these materials in the coming years and to evaluate the sustainability of such an investment.

Among the WEEE (Waste from Electrical and Electronic Equipment), PCBs are an essential part of almost every electronic equipment, being used to mechanically support and electrically connect the various electronic components. The estimated Compound Annual Growth Rate (CAGR) for the PCBs market during the period from 2022 to 2028 is 1.65% [12]. From 2023 to 2030, the PCBs market will cover consumer electronics, communication, aerospace, automotive, industrial electronics, and healthcare. The annual generation of e-waste is rising by 2.6 million tonnes annually, on track to reach 82 million tonnes by 2030 [13]. The management of PCB waste requires a comprehensive approach involving producers, governments, consumers, and international organizations. The transition to a circular economy, public education, promotion of reconditioning, and eco-design are all crucial elements in effectively addressing this challenge and minimizing the environmental impact of this waste. Improving recycling can also help secure the supply of critical raw materials, ultimately enhancing the EU's strategic autonomy from countries with a monopoly on certain materials.

The automotive sector and the mass electronics sector are among the most important sources of PCBs. Car PCBs are complex circuit systems used to control most electronic operations.





Moreover, they are used in the automotive, consisting of printed pathways connecting multiple electronic components. PCBs are adopted in several automotive applications, such as entertainment and navigation systems, brake systems, combimeters, exterior mirrors, rain sensors, speed sensors, and air quality sensors.

A vehicle requires more than 50 metals, including precious, critical, and rare earth metals. Due to a complex set of barriers, such as the disassembly of car parts and the lack of regulations in the sector, the recycling of these metals, which is so crucial for the circular economy, has always been neglected. Remarkable is the lack of interest of car manufacturers that have historically had towards recovering these valuable components from ELVs.

The ongoing shift towards BEVs necessitates an assessment of the impact on mineral usage. BEV sales worldwide increased by 40% in 2020, counting around 3 million vehicles and capturing a market share of over 4%. This has led to a global fleet of over 10 million BEVs. According to the sustainable development scenario, electric car sales are projected to surpass 70 million by 2040 (Figure 33), accompanied by the rapid electrification of light commercial vehicles, buses, and freight trucks.



Figure 33. Annual electric car sales in the sustainable development scenario 2020-2040 [14].



Figure 34 shows minerals used in electric cars (BEV) compared to conventional cars (IEV).





Based on the findings in Figure 34, it's clear that BEVs require a greater amount of minerals. The amount of metals required is reported regardless of the compound in which they are used. Specifically, the demand for minerals used in batteries, such as copper, nickel, manganese, cobalt, and graphite, is expected to increase significantly. Currently, copper is recovered through hydrometallurgical processes developed under the EU Treasure project, while research projects are underway at UNIVAQ for the development of a hydrometallurgical process aimed at recovering lithium. The hydrometallurgical route is the only option for lithium recovery, as the lithium content in the electrolyte solution needs to be volatilized through heat treatments. Additionally, UNIVAQ is involved in the EU Life Graphirec project for the recovery of graphite from the battery anode. It is crucial to promote the recycling of these metals to reduce the economic dependence of Europe on other countries.

Gold's role in BEVs may not be as significant as that of lithium or copper, but it is noteworthy. Due to its excellent conductivity and resistance to corrosion, gold is used in small quantities in specific electronic components. In BEVs, gold can be found in high-reliability connectors, switches, and even in some airbag deployment systems. It is also used in the control units that manage the battery system and other advanced functions. Gold is also used in the sensors deployed in BEVs, particularly in highly sensitive or critical applications where reliability is paramount. In conclusion, while the spotlight often falls on lithium, cobalt, and nickel, it's clear that a diverse cast of precious metals works together to power electric vehicles. From the power-dense lithium-ion batteries to the advanced electronics and powerful motors, these metals are the unsung heroes of the EV revolution, propelling us toward a cleaner, greener future.

The global demand for gold reached 4,448.3 metric tons in 2023, showing a 6% increase from 2010 to 2023. Gold trading is a complex and constantly evolving process that allows for continuous trading across different time zones. Major gold trading centers include the London OTC market, the US futures market, and the Shanghai Gold Exchange (SGE), which collectively account for over 90% of global trade volumes [16]. While China is the largest producer of refined gold, its production is not significantly higher than that of other producers. Australia holds the most significant gold deposits, contributing to around 20% of the global total.

2.3 Recycling of indium-tin oxide glass from liquid crystal displays

The following paragraph summarizes the results of tests conducted on the hydrometallurgical recycling of indium from ITO glass of LCDs. The tests were carried out using the reconfigured pilot plant with the main objectives being to identify any potential issues during the scale-up process and to validate a more sustainable process, mainly from a water use perspective, compared to the one described in D5.4 (ANNEX4).

LCDs and ITO glass are extensively used in the automotive industry. They are integrated into various components of modern cars to enhance functionality, safety, and the overall driving experience. LCDs are used in infotainment systems, instrument clusters (such as digital dashboards), head-up displays, climate control panels, rear-seat entertainment systems, side mirror displays, navigation systems, control interfaces, and smart rearview mirrors. All of these components use indium, which was removed by the European Commission from the list of critical raw materials in 2023 [17]. However, it is still essential to recover it because mineral resources are limited. Therefore, adopting an economically circular approach in the automotive sector, the recycling of LCDs is of fundamental importance.





2.3.1 Pilot tests

Pilot scale tests were carried out using ITO glass samples provided by EUROLCDs. Specifically, UNIVAQ received approximately 15-20 kg of material, cut into 2 cm pieces per side. This material comprised a glass substrate coated with indium and tin oxide layer of 350±30nm thick on both sides. The layer of indium oxide and tin is contaminated by liquid crystals. The sample used for testing is from a supplier (EUROLCDs) and is not actually an end-of-life product. However, the hydrometallurgical process is also suitable for treating ITO glass from ELVs.

The sample underwent characterization to determine the indium and tin content. The results of the sample used for the laboratory tests were almost confirmed on this sample for pilot tests, with a concentration of 1324 g/t of indium and 186 g/t of tin.

The following are the operating conditions reported from tests conducted on a pilot scale. The initial operation involves washing ITO glass to remove liquid crystals. As discussed in D5.4 - ANNEX 4, this washing operation is necessary to prevent the liquid crystals from impeding the recovery of indium from the acid solution in which it was dissolved. The washing operation was carried out under the following conditions: solid concentration of 30% wt./v, room temperature, and a contact time of 1 hour. Acid leaching for selective indium dissolution was then carried out under the following conditions: solid concentration of 15% wt./v, H₂SO₄ 0.1 mol/L, reaction temperature 60°C, and reaction time 1 hour. The leaching operation was tested using a multistage counter-current leaching process. Electrodeposition was then performed for the recovery of indium from the leach liquor solution at the following conditions: voltage 2.5 V, current density 50 A/m², graphite as cathode, and titanium coated by a mixture of oxides as anode. The solution from which the indium was recovered was tested for 80% reuse within the leaching process at the pilot scale. Additionally, a sample of the remaining solution was used for the laboratory-scale study of wastewater treatment.

The equipment used in the pilot plant for the tests is described briefly below. The chemical reactor used for washing and leaching operations was called R103, selected based on the type of material. This reactor is built in polypropylene, equipped with a septum to retain the ITO glass pieces and prevent their discharge during the separation of the leach liquor rich in indium obtained from the chemical reaction. Filtration of small particles that could be detached was performed using cartridge filters with a 10 μ m porous nylon filter. Additionally, during the leaching process, hot water is sent to the reactor via a boiler, and the solution is heated to 60°C using a coil placed inside the reactor. The reactor has a capacity of 100 liters. The chemical reactor R102 was used for the preparation of the leach liquor, the electrolytic cell (CE102) was used. Samples of both solutions and solids were taken during the operations for careful analysis of the process efficiency.

The test consisted of the following operations:

- 1. Load of ITO glass samples into the chemical reactor R103.
- 2. Add water into chemical reactor R102 for the washing.
- 3. Filter and discharge the washing water into a tank.
- 4. Prepare the leaching system in the chemical reactor R102.
- 5. Load the solution in contact with the solid into the chemical reactor R103.
- 6. Allow for the chemical reaction to occur in R103.
- 7. Filter and discharge the leach liquor into R102.
- 8. Repeat steps from 4 to 7 per three times.





- 9. Filter and discharge the final leach liquor into a tank.
- 10. Load the leach liquor solution into the electrolytic cell CE 102.
- 11. Set the rectifier voltage.
- 12. Begin the electrodeposition stage.
- 13. Discharge the solution into a tank and recover the cathode with the indium deposit.

Figure 35 shows the counter-current leaching scheme used in the leaching operations. The process involves three stages of leaching, with the reuse of solutions to increase the concentration of indium. This makes its recovery easier and reduces the consumption of freshwater and reagents. This method, based on lab-scale results, has also allowed for maximizing indium extraction and reducing tin extraction.



Figure 35. Multistage counter-current leaching scheme for selective dissolution of indium from ITO glass, tested at pilot scale.

Table 49 presents the results for each step and cycle, including the concentration and total recovery of indium and tin per cycle. To conduct each cycle, 6 kg of ITO glass was used, and after each cycle, a portion of the remaining solid was chemically analyzed to determine the remaining amounts of indium and tin. This analysis was used to calculate the yields of extraction and the reconstituted feed.

cycle		1 st step	2 nd step	3 rd step	Total recovery
1 st	In, mg/L	105.0	68.0	24.8	In 99.8%
	Sn, mg/L	3.9	1.6	0.6	Sn 20.5%
2 nd	In, mg/L	140.3	81.6	65.9	In 99.4%
	Sn, mg/L	3.4	1.9	1.6	Sn 19.1%
3 rd	In, mg/L	145.4	124.5	74.0	In 99.5%
	Sn, mg/L	3.6	2.9	2.0	Sn 18.3%

Table 49: Counter current leaching process results at pilot scale.





The first cycle involves using 0.1 mol/L sulfuric acid solutions in each of the three steps. In the second and third cycles, solutions from the previous cycles are reused, while in the third step, a fresh leaching solution is used. The solution in the first step becomes increasingly enriched in indium as a function of the cycle, making it easier to recover from the solution. In the third cycle, the indium concentration in the first step achieved 145 mg/L, and it is likely that this concentration could increase in the fourth cycle. The recovery of indium in the third cycle was found to be 99.5%, while the tin recovery was 18.3%. The laboratory scale results demonstrated that the process allows for almost selective recovery of indium, and these results were now confirmed on a pilot scale. Additionally, the concentration gap between indium and tin in the solution sent for electrodeposition (In 145.4 mg/L and Sn 3.6 mg/L) is facilitated by the fact that the tin content in ITO glass samples is considerably lower than the indium content. This testing process also enabled the determination of tin and indium content for each 6 kg batch. In detail, an ITO glass sample with an indium concentration of 1321 g/t and tin of 198 g/t was processed in the first cycle, in the second cycle indium was 1335 g/t and tin 177 g/t, while for the third cycle indium 1316 g/t and tin 183 g/t.



Figure 36 shows a picture of the test carried out in the chemical reactor R103.



The solution obtained from the first step of the third cycle was used for electrodeposition testing using cell CE102 to selectively recover indium. Figure 37 shows the indium recovery and current efficiency over time. The test was carried out at 2.5 V with a current density of approximately 50 A/m².





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Figure 37. Indium electrodeposition at pilot scale, indium recovery vs current efficiency as a function of time.

Based on the results, it is evident that the best conditions by considering both indium recovery and current efficiency are obtained at approximately 2 hours. Electrodeposition for up to 2 hours yields an indium recovery slightly above 80% while maintaining a current efficiency not lower than 17-18%. It is advisable to stop the electrodeposition at 2 hours as the solution is recirculated for 80% in the counter-current leaching operation, allowing for the recovery of most of the indium not retrieved during this test at a later stage. Although it requires greater energy consumption, at 4 hours, 99.2% of indium was recovered from the solution. Therefore, for the overall estimate of indium recovery, it has been decided to consider the recovery obtained at 4 hours. Energy consumption at this condition is 18 kWh per kilogram of recovered indium.

The indium powder deposited on the graphite cathode was carefully collected manually and then analyzed using XRD to confirm the presence of metallic indium. A portion of the collected powder was then subjected to acid chemical analysis using ICP-OES to determine the purity of the indium and to identify any impurities. Figure 38 shows the spectrum of indium obtained by XRD analysis.



Figure 38. XRD analysis on the indium powder obtained by the pilot plant.

From the spectrum, we can observe the main peaks of metallic indium, confirming the presence of indium in metallic form in the powder recovered by electrodeposition.

Quantitative analysis using ICP-OES revealed a 99.3% purity of indium. The main impurity is approximately 0.5-0.6% tin, with traces of calcium sulfate also detected.

The residual solution after indium recovery was reused for 80% to perform a leaching test on a new ITO glass sample. Titration confirmed a slight increase in free acidity, which helped reduce the consumption of sulfuric acid even further. The results of the leaching test aligned with the findings from previous tests shown in Table 49.

As regards wastewater treatment, a sample was taken from the effluent produced after washing the ITO glass with water to remove liquid crystals, as well as a sample of the acid solution obtained after recovering indium by electrodeposition. These two solutions were combined in defined ratios to test the treatment of this wastewater on a laboratory scale.

The effluent from the washing of the ITO glass, after being reused 5 times, has accumulated liquid crystals, resulting in a COD value of 1467 mg/L. The wastewater from the electrodeposition process has a sulfuric acid concentration of 0.05 mol/L, tin concentration of 2.7 mg/L, and indium concentration of 1.3 mg/L. No trace of other metals has been detected. It





is important to note that only 20% of this wastewater is purged and then sent to the wastewater treatment section. Referring to one ton of ITO glass to be treated corresponds to a quantity of wastewater equal to 1335.9 kg, while the washing water amounts to 671.1 kg. Mixing these wastes in a 2:1 ratio resulted in the solution for the tests.

The test consisted of treating the wastewater with lime until it reached a neutral pH level to remove contaminants and obtain reusable water. The consumption of lime (10% wt./v) was 56.2 kg/m³ to reach a pH of 7.5. The test was conducted with agitation at room temperature, and the suspension was filtered using a 5-micron nitrocellulose filter. The results for the water quality and sludge characteristics are provided in Table 50.

Table 50: Outputs obtained by the wastewater treatment.

Treated water	Wet sludge (180 kg/m³)
pH 7.5 COD 257 mg/L In 0.5 mg/L Sn < 0.1 mg/L sulphates	calcium sulphates calcium hydroxide

This process has allowed a significant reduction of the organic load, and the qualitative characteristics of the water are therefore suitable for reuse in the plant as water for washing or other applications. If there are no uses and you want to discharge, it is possible to have a direct discharge in sewage systems at a low cost since the parameters allow it. As for the sludge, it is necessary to dispose of it through specialized external companies, but in any case, being made up almost entirely of calcium sulphates with few pollutants, the disposal costs will not be high.

Furthermore, additional assessments were conducted on the solid residue resulting from the leaching process to obtain a secondary product that can be reused. UNIVAQ has reached out to several organizations and companies to explore the potential for reusing glass after the removal of liquid crystals and indium.

2.3.2 Process analysis

This paragraph illustrates the process flow diagram and provides a full description of the various operations, based on the validation tests conducted at the pilot scale. Additionally, the description of the mass and energy balances, as well as the main results in terms of indium recovery and the purity of the obtained powder are provided.

The flowsheet of the developed process is shown in Figure 39. The hydrometallurgical process, validated on samples supplied by EUROLCDs, aimed at selectively recovering indium from ITO glass of LCDs according to an MLD approach.







Figure 39. Flowsheet of the hydrometallurgical process for the recycling of In from ITO glass.

The hydrometallurgical process is composed of initially washing the ITO glass, followed by the acid dissolution of indium, its recovery through electrodeposition, and a subsequent wastewater treatment phase. Counter-current leaching, reusing solutions in the same operations, and the wastewater treatment section allowed for obtaining a process with low freshwater use according to the principles of the MLD approach.

The ITO glass is preliminary washed with water to remove liquid crystals. This step is crucial to prevent any negative impact on the recovery stage of indium from the leach liquor. The water can be reused for washing up to 5 times before being discharged to the wastewater treatment section.

To dissolve indium, the cleaned ITO glass underwent a multistage counter-current leaching (solid-liquid extraction) process. It consists of three steps using a leaching solution of sulfuric acid (0.1 mol/L) that must be performed at 60 °C. The chemical reaction is below reported:

$$\ln_2 O_3 + 3H_2 SO_4 \rightarrow \ln_2 (SO_4)_3 + 3H_2 O \tag{6}$$

Fresh leaching solution enters from one side (third step), and fresh solid (ITO glass) enters from the opposite side. The main advantages are a more efficient use of reagents and highly concentrated leach liquor from each it is easier to recover the indium in the next phase.

Electrodeposition occurs at the following operative conditions: voltage 2.5 V, current density 50 A/m², graphite as cathode material, and titanium coated by a mixed oxide as anode. The indium metal powder has been recovered with a purity of 99.3%; impurities are due to tin and calcium sulphate. By exploiting the increasing free acidity after electrodeposition, it is possible to recycle





up to 80% of the solution discharged from indium. This recycling can be done in the countercurrent leaching section, with partial sulfuric acid make-up (50%). This approach reduces waste and environmental impact and saves costs, leading to a more profitable process. The remaining 20% of the solution and the water used to wash the ITO glass are sent to the wastewater section. The wastewater treatment process involves adding lime to neutralize the solution and transferring the pollutants in the sludges. This results in a water quality that meets the standard for direct discharge to sewerage at low costs. Additionally, the treated water can be reused within the plant if necessary.

Water consumption of the process is 1960.3 kg per 1 ton of ITO glass, resulting in a water footprint of 1440.5 kg of water/kg indium product.

Table 51 shows the efficiency of the process in terms of indium recovery for both leaching and electrodeposition. The indium recovery in the leaching is 99.5%; it is the results of the third cycle that it is the cycle among those investigated that has reached more the conditions of the regime according to the adopted scheme in counter current. The electrodeposition efficiency as indium recovery was 99.2%. Therefore, the overall indium recovery of the process was 98.7%. The table also reports the recoveries of tin in the various phases. Since indium contributes to more than 95% of ITO glass's intrinsic economic value, the goal was to selectively recover only indium to obtain a final product with a higher indium grade. Therefore, achieving only a 4.4% recovery of the tin is certainly a good result.

	Recov	/ery
stage	In, %	Sn, %
Washing	0.0	0.0
Counter-current leaching	99.5	18.3
Indium electrodeposition	99.2	24.0
overall	98.7	4.4

Table 51. Results obtained by the validation pilot plant test, indium and tin extraction yields.

Table 52 presents the mass balance based on the results obtained in the pilot-scale validation process. The calculations refer to the processing of a ton of ITO glass. The average initial concentration of tin in the ITO glass was 1324 ± 10 g/t.

Table 52. Mass balance of the process for the recycling of indium from 1 ton of ITO glass based on the results obtained at pilot scale.

Input, kg		Output, kg	
ITO glass	1000.0	dry solid/secondary product	938.0
water	1960.3	indium powder	1.316
sulfuric acid, 50 %	79.9	humidity	93.9
lime, 10%	109.5	treated water to sewerage	1842.2
-	-	wet sludges	292.3
	3149.7		3149.7





The mass balance indicates that from one ton of ITO glass, 1.316 kg of indium powder can be recovered, along with 938 kg of a secondary product composed of glass. The water usage was reduced compared to the lab-scale tests (D5.4 – ANNEX 4) to create a more sustainable process. The consumption of sulfuric acid is really very low (79.9 kg per ton of ITO glass) thanks to the adoption of the counter-current leaching scheme and thanks to the reuse of 80% of the solution after electrodeposition in which a certain amount of sulfuric acid is still present.

The process outputs have been characterized to primarily highlight the purity of the products obtained and the chemical composition of the other outputs for proper management. Table 53 presents the purity and form of indium in the obtained powder, in addition to the main

detected impurities. Analyses were conducted using XRD and ICP-OES analysis after specific chemical treatments.

	Indium powder
form	metal
purity, wt. %	99.3
impurities	Sn 0.58%, traces of calcium sulphate

Table 53: Chemical composition of the indium powder obtained by the process.

Indium is obtained in its metallic form, as confirmed by the spectrum obtained by XRD analysis shown in Figure 38, with a purity of 99.3%. The impurities consist of 0.58% tin, along with traces of calcium sulfate due to aqueous residues of sulfuric acid.

Regarding the other outputs, "dry solid residue/secondary product" refers to the leaching solid residue. From one ton, 938 kg of this fraction is obtained. The dry solid is composed of essentially glass, with a residual of not dissolved tin. The chemical composition is detailed in Table 54, and the analysis results are obtained from various techniques including XRF, XRD, and ICP-OES.

Dry solid residue/secondary product characterization	
SiO ₂ , wt. %	74.8
Na₂O, wt. %	10.9
CaO, wt. %	8.4
MgO, wt. %	2.8
Al ₂ O ₃ , wt. %	1.6
K ₂ O, wt. %	0.8
Fe ₂ O ₃ , wt. %	0.1
SnO ₂ , g/t	173

Table 54: Dry solid residue/secondary product of indium recycling process characterization.

For better sustainability of the developed process, it is crucial to evaluate the possibility of reusing this fraction to produce glass since it constitutes 93.8% of the weight of the initial sample processed.

Online meetings were organized between UNIVAQ and EUROLCDs to discuss the potential reuse of glass following the hydrometallurgical recycling process. Unfortunately, EUROLCDs could not





effectively test this possibility due to the high batch quantities it uses to produce LCDs in comparison to the quantities available after the tests conducted by UNIVAQ on a pilot scale. However, EUROLCDs provided a list of their contacts to UNIVAQ to assess this option. Although there were these contacts, it was not possible to test the reuse. UNIVAQ has conducted additional studies at the national level, reaching out to SMEs, some of whom have shown strong interest. Contacts are ongoing, and the potential for glass reuse will likely be tested in the coming months.

The output "humidity" refers to the water that remains on the solid after separating the leach liquor solution from the solid and to the water associated with the indium powder.

The other outputs, "treated water" and "wet sludges," are obtained from the wastewater treatment section. Their characteristics are reported in Table 55.

Table 55: Treated water and wet sludges composition.

Treated water	Wet sludge
pH 7.5 COD 257 mg/L In 0.5 mg/L Sn < 0.1 mg/L sulphates	calcium sulphates calcium hydroxide

The treated water meets high-quality standards, with COD levels below regulatory limits and no metals detected above the allowable thresholds. As a result, it is suitable for discharge into sewage plants or can be reused for washing residual solids from the hydrometallurgical process. The sludge from the lime treatment process obtained from the wastewater treatment section primarily consists of calcium sulfate and trace of pollutants, as the liquid crystal substances are transferred to this sludge. This sludge must be disposed of by specialized companies.

Based on the material balance determined through tests conducted at the pilot scale, it was possible to evaluate the economic feasibility of the process.

Table 56 reports the OPEX by considering the quantities of chemicals used to treat 1 ton of ITO glass, disposal costs for residual solids and solutions, and energy consumption.

Table 56: Chemical consumption and other costs for the treatment of 1 ton of ITO glass.

Chemical	Amount, kg	Cost per unit, €/kg	Cost, €
H ₂ SO ₄ (50% w/v)	79.9	0.13	10.4
Water	1960.3	0.0015	2.9
Lime (10% w/v)	109.5	0.015	1.6
			14.9€
Output	Amount, kg	Cost per unit, €/kg	Cost, €
Output Dry solid residue/secondary product	Amount, kg 938.0	Cost per unit, €/kg 0.0	Cost, € 0.0
Output Dry solid residue/secondary product Treated water to sewerage	Amount, kg 938.0 1842.2	Cost per unit, €/kg 0.0 0.0005	Cost, € 0.0 0.92
Output Dry solid residue/secondary product Treated water to sewerage Wet sludge	Amount, kg 938.0 1842.2 292.3	Cost per unit, €/kg 0.0 0.0005 0.08	Cost, € 0.0 0.92 23.38





Operation	Energy consumption, kWh	Cost per unit, €/kWh	Cost, €
Stirring	20	0.40	8.0
Pumps	24	0.40	9.6
Reactor heating at 60°C for the leaching	257.3	0.40	102.9
In electrodeposition (18 kWh/kg)	23.7	0.40	9.5
			130.0€
OPEX			169.2 €

The total cost for the reagents is $14.9 \in$, which is surprisingly low compared to what is typically required for a hydrometallurgical process. This was made possible through experimentation on a laboratory scale within Task 5.4, which maximized the recovery of indium while minimizing the consumption of sulfuric acid. Additionally, the reuse of solutions through a countercurrent regime and the reuse of the solution after electrodeposition, which still contains a certain amount of sulfuric acid, also contributed to this excellent result.

For the management of solid waste and residual solutions, it's crucial to explore the potential for reusing the secondary product in glass production. UNIVAQ will conduct further investigations to assess this possibility. Currently, it's considered an output that doesn't incur disposal costs or generate revenue. Overall, the disposal of solids and residual solutions, assuming the treated water is sent to the sewer, amounts to a total cost of $24.3 \in$.

The highest operating costs are related to energy consumption, totalling ≤ 130 for treating one ton of ITO glass. The largest cost comes from the energy needed to heat the reactor to 60°C for dissolving indium through the counter-current leaching process. Overall, OPEX amounted to ≤ 169.2 .

The costs for separating ITO glass from the rest of the LCDs and reducing ITO glass into pieces for the hydrometallurgical process still need to be considered with respect to the calculated OPEX. The size of the ITO glass pieces may vary based on the construction characteristics of the leaching reactor for industrial-scale implementation. Additionally, costs related to operators are not estimated since they will depend on plant capacity, work shifts, and location of the plant.

The only source of revenue is the indium metal powder recovered from the recycling process, so the economic feasibility of the process depends heavily on the economic value of the indium. To ensure greater stability and avoid economic analysis during peak periods, the economic value of indium has been calculated based on the average value of the last 5 years, which is 394.75 ξ/kg [18]. In addition, the economic value has been depreciated based on the percentage of purity in the obtained product.

However, this is just an economic estimate; the effective sustainability will be determined by the agreements that the industrial plant's owner can establish with any end users of the metal indium.

Based on these considerations, Table 57 reports the OPEX and revenues for the treatment of 1 ton of ITO glass.





Item	Cost, €	Revenues, €
Chemicals	14.9	
Energy consumption in the recycling process	130.0	
Solid waste and residual solution management	24.3	
Indium (purity 99.3%), value 391.99 €/kg		515.9
profit per ton of ITO glass		+ 346.7 €

Table 57: OPEX and revenues for the treatment of 1 ton of ITO glass.

The preliminary economic analysis shows that this process for the hydrometallurgical recycling of indium can guarantee an annual profit of \notin 346.7. Given the gap not so high between OPEX and revenues, the economic feasibility of the process remains at the limit. Specifically, it is highly dependent on the indium content in ITO glass. A small analysis was conducted to determine the break-even point in terms of indium content, which is the value at which revenues and costs are equal. Considering the efficiency of the process in terms of indium recovery and the purity of the product obtained the break-even point is reached at a concentration of indium in ITO glass equal to 435 g/t. This is a significant margin, considering that it is over 65% less than the indium content of the ITO glass on which the hydrometallurgical process as a secondary product in glass production remains to be confirmed. This open point inevitably affects the results of the preliminary economic analysis.

2.3.3 Discussion

The hydrometallurgical process for recycling indium from ITO glass of LCDs has been successfully tested on a pilot scale. The results confirmed that the implemented process is feasible by a technical-economic point of view and sustainable from a water use perspective. The adoption of the MLD approach helped to reduce the use of freshwater and chemicals. The main methods used were counter-current leaching and reusing the solutions after recovering the indium. Additionally, the introduction of a wastewater treatment section helped to enhance the environmental impact of the process by avoiding wastewater production and also proved to be economically beneficial.

The main strengths of the developed process are as follows:

- The best leaching conditions were identified to maximize indium dissolution (99.5%) and minimize tin dissolution (18.3%), resulting in a high-purity indium product (99.3%). This outcome was achieved through factorial experimentation conducted on a laboratory scale in Task 5.4, and the results were then validated on a pilot scale.
- The use of counter-current leaching and the reuse of the indium recovery solution make the process more efficient by reducing the need for reagents and freshwater. Specifically, treating 1 ton of ITO glass requires only 79.9 kg of 50% sulfuric acid, and the water footprint is 1440.5 kg of water per kilogram of recycled indium.
- The implementation of a dedicated wastewater treatment section resulted in reduced disposal costs and the achievement of zero contaminated wastewater discharges.

Some potentially critical aspects or open points are the following:





- The actual costs for reducing the size of ITO glass to make it suitable for the hydrometallurgical process remain uncertain. EUROLCDs spent a significant amount of time preparing the material by cutting it. It is evident that an alternative method for preparing the material without the need for operators' efforts would be necessary.
- To ensure the sustainability of the process, the leaching solid residue, mainly consisting of glass with residual tin, must be managed as a secondary product for glass production. A series of contacts is underway with interested glass manufacturers to investigate the reuse options.
- The concentration of indium in ITO glass varies depending on the specific applications in which LCDs are used. A concentration of indium higher than 435 g/t is necessary for the economic feasibility of the process.

The results of the pilot-scale recycling process have been validated and found to be satisfactory. Additionally, the current and future availability of LCDs, as well as the strategic value of recovering indium, are significant. For these reasons, **UNIVAQ has decided to protect this technology by including it in the patent proposal submitted** for the recycling of silver from IME.

Below is a brief analysis of the availability of LCDs in the automotive sector as well as the demand for indium.

The global automotive LCD market is expected to experience significant growth, with an estimated CAGR of 7.48% from 2024 to 2031 [19]. The growing demand for infotainment systems in automobiles is a major factor driving the growth of the automotive display market. Consumers are increasingly seeking advanced and sophisticated infotainment systems in their vehicles, leading to a higher demand for larger, high-resolution displays and advanced features. This trend is spurring innovation and fostering growth in the automotive display market.

Indium was included in the Critical Raw Materials (CRM) list when it was first published in 2011. However, it was no longer included in the fifth list published in 2023 [16]. It was removed from the EU list of CRMs because the EU has sufficient domestic production to meet its needs. However, the high-grade indium is mainly produced outside of the EU, with China, Japan, and Canada being the main producers. Indium is typically extracted through mining and refining processes. Estimating reserves of indium is challenging because it is a byproduct commodity that comes from a wide variety of zinc-rich ore deposit types. China holds over 50% of indium production, with other leading producers being the Republic of Korea, Japan, Canada, and Belgium. These five countries collectively account for almost 95% of primary indium production. Indium is used in touch screens, flat-screen TVs, photovoltaic cells, and batteries, making it important for enabling low-carbon energy solutions in the EU economy. This contributes to achieving the objectives of the "European strategic long-term vision for a prosperous, modern, competitive, and climate-neutral economy." Considering the above and the socio-economic importance of these applications, it is evident that indium holds strategic value for Europe.

In this context, adopting the hydrometallurgical recycling process for recovering indium metal will significantly reduce the need for mineral extraction and its associated environmental impacts, thereby safeguarding valuable mineral resources. The primary goal is to create closing materials loops, ensuring that indium recovered through this process is reused directly in the production of ITO glass. Preliminary discussions with EUROLCDs have been initiated, and ongoing contacts with their ITO glass suppliers aim to evaluate the feasibility of direct reuse.





3. Training activities

UNIVAQ personnel conducted training for ILSSA on operating the hydrometallurgical pilot plant on 13th November 2023. This activity is crucial as it connects research activities, validated on a pilot scale by UNIVAQ, with the needs of end users, represented in this context by ILSSA.

3.1 Training program

The training program focuses on conducting hydrometallurgical processes and following safety procedures. In more detail, here are the activities included in the training program:

- Introduction to hydrometallurgical processes at the University of L'Aquila (L'Aquila, Italy)
 - Visit of the "Laboratory of Mechanical Physical Treatments" for the preparation of the material to be subjected to hydrometallurgical recycling (operation of the cutting mill – Retsch SM300 and practices for disassembly).
 - Visit of the "Development process laboratory for industrial waste treatment and integrated wastewater treatment."
 - Chemical characterization of the sample for the determination of intrinsic economic value (execution of quartering, methods for acid mineralization of solid samples and ICP/OES spectroscopy).
 - Execution of the main operations that are included in the hydrometallurgical processes (preparation of leaching solutions, solid/liquid extraction – leaching, filtration, centrifugation, selective recovery of the metals from the leach liquor by electrodeposition, precipitation and chemical cementation).
 - Explanation of the hydrometallurgical processes developed within the EU project Treasure and presentation of the pilot plant.
- Use of the hydrometallurgical pilot plant at Lorusso Estrazione Srl (Avezzano, Italy)
 - Illustration of the different areas of the hydrometallurgical pilot plant: chemical storage area, temporary solution storage, operational area, and control panel area. Visit of the quality laboratory and service control of the plant.
 - Explanation of the different equipment needed for the execution of the hydrometallurgical process for the treatment of electronic board powders (chemical reactor R102 and R103, bag and cartridge filtration systems, temperature and weight controls, electrolytic cells).
 - Explanation of the use of automation in the pilot plant via PLC software (training on the use of the software for the execution of the recorded processes and for the insertion of new operations).
 - Safety practices and plant maintenance, use of individual protection devices (acid-resistant gloves, acid-resistant workwear, chemical safety goggles, chemical/dust mask respirator, and protective/acid-resistant safety shoes).
 - Preparation of the materials to be subjected to the hydrometallurgical recycling process (powders of PCBs).
 - Ignition of the plant from the electrical cabinet and activation of the scrubber to reduce gaseous emissions after checking the measure of pH in the soda bath for neutralization.
 - Leaching of metals by using the chemical reactor R102 (loading of the chemicals and of the powders).





- Filtration operation by using the filter bag FC201 (discharge of the leach liquor 0 into a temporary tank and washing of the solid residue).
- o Electrodeposition of copper by using the electrolytic cell (insert of copper cathode and titanium anodes, loading of the leach liquor in the bath, switch on of the rectifier and of the recirculating pump).
- Shut down the plant, washing, and cleaning all the used equipment for good 0 maintenance practices.

Figure 40 shows some images of the training day at the University of L'Aquila and at the hydrometallurgical pilot plant located in Avezzano.





Figure 40. ILSSA and UNIVAQ personnel in front of the chemistry laboratory building at the University of L'Aquila (left side), and ILSSA during the training in the hydrometallurgical pilot plant at Avezzano (right side).

After completing this training, ILSSA gained knowledge about hydrometallurgical processes, which it then shared with all the operators in the company. This phase is crucial because ILSSA, as an end-user of the hydrometallurgical technologies developed by UNIVAQ, can assess the benefits of these processes compared to the current material management practices at ILSSA as a waste disposer and automotive dismantler.

3.2 Operating and Maintenance Handbook

The training material consists of an operating, maintenance, and safety manual for the use of the hydrometallurgical pilot plant.

The manual includes a detailed description of the pilot plant and its various equipment such as chemical reactors, reagent storage tanks, filtration systems, electrolytic cells, and the level of automation via PLC governed by the control panel area. It also covers the procedures for the correct start-up of the pilot plant before conducting any tests and the operations to be performed by the PLC for executing various hydrometallurgical processes developed and validated within the activities of the EU Treasure project. The manual serves as a guide for operators. The operating and maintenance handbook is included as an **ANNEX** to D6.2.





3.3 Benefits of the developed hydrometallurgical technologies

In this section, ILSSA presents its perspective following the training on hydrometallurgical processes and the use of the pilot plant.

ILSSA compared their current management of material flows with the potential benefits of adopting hydrometallurgical processes in their company. This perspective is crucial as it highlights the advantages and challenges for end users in utilizing the technologies developed within the EU Treasure project for the hydrometallurgical recycling of various metals from different types of automotive waste.

ILSSA explains that in the automotive industry, traditional material recovery involves processes such as physically recycling metals from scrapped vehicles or reusing components. Circular economy approaches in the automotive industry aim to surpass traditional recovery methods by focusing on design for disassembly, remanufacturing, and using recycled materials in manufacturing. This reduces waste and energy consumption while extending the life cycle of automotive products. Metals can be reused through various processes such as recycling, remanufacturing, and reusing. Recycling involves melting down metals to create new products, while remanufacturing involves refurbishing components to a like-new condition. Reusing involves using metals for different applications than their original purpose. These methods contribute to the circular economy by reducing the need for virgin materials and minimizing waste.

Comparing the two industrial recovery processes in terms of circularity involves assessing their ability to recover and reuse materials efficiently, minimizing waste and environmental impact. If we compare the process that ILSSA is using now with the one that we have obtained from the investigation of UNIVAQ to recover the materials, we have the following results reported as a function of different aspects.

Material input and sourcing

ILSSA: We receive the cars in our facilities. We can have various origins: old vehicles that no longer work, vehicles from accidents, or vehicles whose owner wants to exchange for a new one but that are still in good condition and can be used. After carrying out decontamination, the parts that can be used are removed.

The disassembly of the parts is carried out at the ILSSA facilities. All components are removed, differentiating between plastics, metal parts and electronic boards. After the selection of the different materials and parts, they are sent to different customers, or they can go to

UNIVAQ: The new metal recovery technique is carried out by crushing the plates, which are then taken to the pilot plant and the metals are extracted through chemical processes. A higher level of material recovery is reached. In this process, we will use the material obtained and will have a reduction of the raw materials for the next component we need to produce and use to join a vehicle.

<u>Resource efficiency</u>

ILSSA: The plastics, the metals and the electronic boards are sold to other companies or are discarded. ILSSA generates significant waste during manufacturing with limited efforts to reuse or recycle byproducts.

UNIVAQ: Implements closed-loop systems or cascading processes to maximize resource efficiency, minimizing waste generation.





<u>Energy consumption</u>

ILSSA: energy consumption is low. Basically, the entire process of reducing the car into pieces is carried out manually, so the energy consumption is low compared to other industrial processes.

UNIVAQ: Integrates energy-saving technologies and renewable energy sources to reduce energy consumption and carbon footprint.

• Product lifetime and End-of-life management

ILSSA: The vehicles arrive at our facilities because they are not going to be used anymore, so very highly efficient management is carried out to obtain the maximum possible materials.

UNIVAQ: They go one step further to try to obtain precious metals that can be reused to make new pieces and avoid the use of raw materials.

• <u>Circular business models</u>

ILSSA: We can say that ILSSA is at the end of linear production, and it tries to recover all possible materials so that they can be reused or recovered. We are one step behind of UNIVAQ. We have provided them with the ground material so that they can process it in their pilot plant, so it falls within the panorama of the circular economy that the Treasure Project wants to develop in the automobile industry.

UNIVAQ: Adopt circular business models, going one step ahead in the circular economy model. They are able of obtaining different metals, carrying out chemical processes on what was initially going to have a very different purpose, because it was possibly going to end up as an unrecovered final waste.

<u>Economic viability</u>

ILSSA: Initially, we have lower production costs, although we may incur higher long-term expenses related to waste disposal and resource depletion, but this may happen in the long term because Spain has a high number of vehicles in its automobile park.

UNIVAQ: This may require higher footprint investments in recycling infrastructure but offers potential cost savings through reduced material costs and enhanced brand reputation.

In conclusion, UNIVAQ demonstrates greater circularity compared to ILSSA by prioritizing resource efficiency, sustainable material sourcing, and circular business practices. By minimizing waste generation, maximizing material reuse, and reducing environmental impact. UNIVAQ aligns more closely with circular economy principles in the automotive sector.





4. Conclusions

The activities conducted under Task 6.2 of the EU Treasure project allowed for testing of the reconfigured hydrometallurgical pilot plant. This confirmed the suitability of the added equipment, making the experimental plant more flexible in treating different types of materials in the automotive industry. Pilot scale testing also validated processes developed and optimized at the laboratory scale. Confirming the efficiency of these processes at this scale allows end users to invest in building industrial plants for hydrometallurgical recycling.

The pilot-scale validated processes are economically feasible and all include a wastewater treatment section that allows for adopting the MLD approach. Additionally, some reagents are partially regenerated, and others are recovered, providing the possibility of reusing the solutions used for leaching. This helps to reduce reagent consumption and lower associated costs. The main results achieved for each of the validated hydrometallurgical processes are listed below:

- Recycling of silver from in-mold electronics:
 - Silver is extracted into solution through a two-stage solid-liquid extraction treatment. In the first stage, thiourea (20 g/L), ferric sulfate (Fe³⁺ 6 g/L), and sulfuric acid (0.2 mol/L) are used as a leaching system. The second stage uses the same solution as the first, with a make-up of reagents according to their consumption.
 - Silver is recovered from the solution in which it was dissolved through electrodeposition (voltage 1.2 V, current density 50 A/m²) using a silver plate as the cathode. During this process, there is a partial regeneration of some reagents (thiourea and free acidity). This innovative aspect allows for a reduction in reagent consumption when reusing the solution for subsequent batches.
 - After three cycles of the recycling process, the solution is sent to a dedicated wastewater section. This section takes advantage of the presence of iron in the wastewater to save this reagent and uses it together with the hydrogen peroxide to perform a Fenton process followed by lime neutralization. The treated water meets quality standards that allow 70% of it to be reused for a new batch.
 - The overall silver recovery is 82.9%, and the purity of the product obtained is 98.6%. The use of fresh water is 464.3 kg per ton of in-mold electronics processed.
 - UNIVAQ has submitted a patent proposal on the hydrometallurgical recycling of silver from in-mold electronics.
 - At the moment, building an industrial plant to recover silver from in-mold electronics is not practical due to the limited availability of these materials. However, the same technology can be used to recycle silver from photovoltaic panels. Therefore, it would be feasible to consider constructing a plant that can initially process photovoltaic panels and then, as the demand for in-mold electronics is expected to increase significantly in the market, could also handle in-mold electronics.
 - The circularity of silver in in-mold electronics has been investigated, based on TNO suggestion. This activity has been tested by GENESINK (a member of AB), which involves using the silver recovered from the hydrometallurgical process as a precursor to producing new silver ink. The aim is to close the loop of the material. However, the results did not show the feasibility of this approach, possibly due to the low purity of the initial silver sample obtained by the pilot. Nevertheless, this investigation paves the way for further activities that could make this approach viable.





- Recycling of printed circuit boards:
 - Some electronic components have been identified for removal from PCBs because their presence inhibits the metal dissolution yields during the hydrometallurgical recycling process. The disassembly of these components has also been tested by POLIMI using COBOT technology. This fraction makes up approximately 15-20% of the total weight and is not suitable for hydrometallurgical recycling.
 - A further breakdown of the residual fraction enables more efficient recycling of PCBs. Two hydrometallurgical routes have been identified for the treatment of PCBs. The first route, based on the Gold-REC 1 patent and optimized subsequently, involves treating PCB powders after reducing them to a particle size of 2 mm. This powder makes up about 80% of the weight of the PCBs. The second route, based on the Gold-REC 2 patent and after further optimizations, involves treating gold-plated electronic components after crushing them to a size of 1 cm, which constitutes about 5% of the weight of the PCBs.
 - Regarding the Gold-REC 1 process, studies have shown that adding a base metal leaching step with a lower dosage of hydrogen peroxide can increase process efficiency and reduce overall hydrogen peroxide consumption.
 - In the Gold-REC 1 process, the reuse of 80% of the solutions has led to a reduction in the consumption of freshwater. Additionally, two wastewater treatment sections have been introduced to ensure that the water meets reuse standards and to prevent the discharge of contaminated wastewater.
 - The Gold-REC 1 process resulted in the following overall recoveries: Au 78.9%, Ag 67.7%, Cu 97.3%, and Sn 91.6%. The purity of the products obtained is as follows: metallic gold 99.1%, silver chloride 99.8%, tin oxide 99.1%, metallic copper 99.4%.
 - The Gold-REC 2 process, with respect to the patented process, includes a preliminary crushing step to increase metal extraction yields and a final three-stage evaporation section to recover hydrochloric acid. This operation helps reduce reagent consumption and wastewater production resulting in only a sludge to be disposed of along with aqueous streams containing hydrochloric acid.
 - The Gold-REC 2 process resulted in the following overall recoveries: Au 93.7%, Ag 72.8%, Pd 38.0%, Cu 88.4%, and Sn 76.0%. The purity of the products obtained is as follows: metallic gold 99.2%, silver chloride 95.0%, metallic palladium 84.9%, metallic tin 96.1%, metallic copper 92.3%.
 - The estimated CAGR for the PCB market indicates an increased demand for mineral resources also due to the growing BEV market. This highlights the necessity to invest in metal recycling processes for secondary materials at an industrial level. To safeguard mineral resources, it is crucial to establish commercial industrial plants for hydrometallurgical recycling.
- Recycling of indium-tin oxide from LCDs:
 - The indium recovery process involves an initial treatment to remove liquid crystals from ITO glass. This treatment uses water, which can be reused up to 5 times before being sent to a dedicated wastewater treatment section.
 - Indium is extracted into solution using a solid/liquid extraction process studied through a counter-current leaching method, which helps reduce reagent consumption and the use of freshwater. It also enriches the solutions in indium, an important aspect for its subsequent recovery. The leaching system uses a very low





concentration of 0.1 mol/L sulfuric acid, but leaching must be carried out at 60°C to allow for the selective recovery of indium.

- Indium is then recovered by electroplating under the following operating conditions: voltage 2.5 V, current density 50 A/m², graphite cathode. 80% of the exhausted solution can be reused in the leaching stage.
- A wastewater treatment section receives both the washing solution that has gone through five treatment cycles and 20% of the solution from which indium has been discharged. The treated water has appropriate quality characteristics to be used again or as a service water in the plant.
- The overall indium recovery is 98.7%, and the purity of the product obtained is 99.3%. The use of freshwater is 1960.3 kg per ton of ITO glass processed.
- The widespread use of LCD displays, especially in the automotive sector, has increased the demand for indium, highlighting the need for its recovery at industrial level. This is due to the growing use of technologies that rely on indium, not only in infotainment systems but also in various other applications in the car. Recognizing the importance of recycling these materials and leveraging developed technology, UNIVAQ has incorporated this recycling process into the patent proposal for inmold electronics.

It is essential to acknowledge and highlight any potential limitations and conduct further investigations when necessary. These investigations are already underway as part of the project to manage the solid residue generated by the hydrometallurgical processes, constituting a significant amount of the total material processed. Specifically, it is important to recover secondary products, such as plastic sheets from the in-mold electronics process, through which the polycarbonate can be recycled after extracting the silver. Additionally, efforts are needed to reuse the solid residue of the recycling process of indium from ITO glass to produce glass. Proper management of these solid residues is crucial to ensure the overall sustainability of the hydrometallurgical processes that have been validated on a pilot scale.

As for the recycling of PCBs, the criticalities in terms of disassembly of the PCBs from different critical car components are to be stressed. This is certainly a limiting aspect, especially because it requires manual efforts on the part of the operators, and the defined disassembly times can increase considerably in case of crashed vehicles. Moreover, the electronic components used in cars vary greatly from model to model, even within the same company. As a result, the metal content in the PCBs also varies significantly. This variability poses a challenge for the sustainability of the recycling process, as it depends on the specific materials present in the car model being recycled. To address this issue, UNI has developed a CEN Workshop Agreement for standardization aimed at tracking electronic components from their manufacturers to the automotive sector. The traceability would simplify the identification of car models that should be the focus of recycling efforts.

Other limitations could arise from the purity of the final products, which should be further increased through specific refining treatments to be carried out on an industrial scale.

UNIZAR assessed the circularity performance of hydrometallurgical processes in D6.4. They considered the adoption of a thermodynamic rarity indicator, and UNIVAQ implemented the recovery of the intrinsic economic value of each material as a further indicator.

Finally, the training for using the hydrometallurgical pilot plant and ILSSA's approach, as a potential end-user, to these technologies have highlighted the benefits that hydrometallurgical recycling could bring to the automotive sector at industrial level. This approach is increasingly in line with the principles of the circular economy.





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Abbreviations

ANOVA	Analysis of Variance
BEV	Battery Electric Vehicle
СОВОТ	Collaborative Robot
COD	Chemical Oxygen Demand
CRM	Critical Raw Materials
ELVs	End-of-Life Vehicles
FTIR	Fourier Transform Infrared
GDR1	Gold-REC 1 patent
GDR2	Gold-REC 2 patent
ICC	Integrated Circuit Chips
ICE	Internal Combustion Engine
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IEV	Intrinsic Economic Value
IMEs	In-mold electronics
ITO	Indium Tin Oxide
KETs	Key Enable Technologies
LED	Light Emitting Diodes
MLD	Minimal Liquid Discharge
OPEX	Operating Expense
P&ID	Process and Instrument Diagram
PCBs	Printed Circuit Boards
SMDs	Surface-Mount Devices
WEEE	Waste from Electrical and Electronic Equipment
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence







D6.2: Report on biohydrometallurgical materials recovery

<u>Annex 1 – Hydrometallurgical Pilot</u> <u>Plant, Operating and Maintenance</u> <u>Handbook</u>

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1. Introduction

The hydrometallurgical pilot plant, Treasure, is situated 50 km from the University of L'Aquila, within an industrial area of a small enterprise (Lorusso Estrazione Srl, Avezzano (AQ), Italy) dedicated to WEEE recycling activities.

The pilot has been ingeniously constructed inside a mobile 40-foot container, a design that allows for its relocation to various SMEs. This mobility serves the purpose of testing and demonstrating the technical feasibility of the hydrometallurgical processes developed in the Treasure project.

The pilot plant is equipped with several units for carrying out various chemical operations. These units include different types of chemical reactors used to process materials of different sizes with water and chemical reactants to dissolve base, precious, and other strategic metals in an operation called leaching. There are also different filtration units for solid-liquid separation after the leaching step, as well as storage tanks to collect the different solutions after filtration. In addition, there are two electrolytic cells for recovering base, precious, and strategic metals by electrodeposition, and a scrubber to maintain air quality for all the unit operations in the pilot plant, including the container areas, for safety and environmental reasons.

The plant is highly automated, with most of the valves and controls being automated according to Industry 4.0 and governed directly by dedicated PLC software from the control panel area. The computer workstation is in an area inside the container but separated from the operating areas where chemical reactions take place. Multiple recipes have been constructed within the PLC based on the materials to be processed. This allows the operator to be fully guided and only enter minimal information to carry out the necessary hydrometallurgical treatments for the recycling process.

The hydrometallurgical pilot plant is an experimental plant at TRL5 that is highly flexible and capable of testing hydrometallurgical operations for treating various materials. It is not suitable for production. This pilot plant is used to scale up processes developed at the laboratory level, allowing for the evaluation of any scale-up-related issues and validation. This step is crucial as it influences investor decisions regarding the potential construction of industrial plants.

The materials tested included electronic board powders, various electronic components such as CPU, RAM, and connectors, in-mold electronics, ITO glass of LCD, photovoltaic panel powders, and catalysts. These materials were used to produce products with high concentrations of gold, silver, tin, copper, and palladium.





2. Plant description

The plant was constructed by BFC Sistemi S.r.l. It has a Declaration of Conformity for the reconfigured plant (serial number 19003, year of construction 2019, and subsequent revamping carried out in 2022) issued, complying with the provisions of European Directive 2006/42/EC [1]. A layout of the hydrometallurgical Treasure pilot plant is shown in Figure 1.



Figure 1. Layout of the hydrometallurgical pilot plant, plan view.

The plant is divided into three different internal areas and one external, starting from the left side:

- 1) Temporary storage for processed solutions and leaching area
- 2) Operating process area
- 3) Control panel area
- 4) Chemical storage area (external to the plant)

The <u>temporary storage of processed solutions and leaching area</u> consists of 6 polypropylene tanks, each with a 200-litre capacity. These tanks are equipped with two adjustable centrifugal pumps for transferring solutions. Their purpose is to temporarily store solutions obtained from the leaching process, which are later recharged into other equipment for selective metal recovery.

In this area, there are two polypropylene chemical reactors used for leaching operations: R102 and R103.

- Chemical Reactor R102 is a slurry reactor designed for treating materials in the form of powders with small particle sizes. It has a useful volume of 100 litres and is equipped with a stirrer (M102) for good suspension mixing. For the discharge operations, a pneumatic diaphragm pump (PP201) allows the suspension to be transferred to the filtration systems. Depending on specific objectives (solid content and particle size), bag (FC201) and cartridge filtration (FC202) systems are in line. It is possible to work with both or decide to exclude one of them. Cartridge filters with different openings can be selected from 0.45µm to 50 µm as well as the filter material (nylon or ceramic). This type of reactor can be used for leaching operations, as well as for preparing solutions, cementations, and precipitations.
- Chemical Reactor R103 is specially designed with a septum at the bottom, consisting of several 1.2 mm openings that allow the passage of solutions while retaining the solid. It





has a useful volume of 100 litres. The advantage is that there is no need to discharge the solid from the reactor to separate it from the solution in which the interested metals were dissolved. A pneumatic diaphragm pump (PP301) was used for the discharge operations. The solid material is discharged through a side door by a rotor with two curved fixed blades. The reactor is equipped with an instant temperature indicator (TIC103) and a weight indicator (WIC103). This reactor is intended for treating materials of larger sizes without the need for grinding or with only a partial reduction in size. It can also be used for heavy powders to prevent clogging.

Both reactors are equipped with a coil to regulate the temperature of the chemical reactions. There are also various level and temperature controls directly displayed via PLC.

In the <u>operating process area</u>, various chemical operations essential for hydrometallurgical processes are performed. Here's an overview of the main equipment used:

- Scrubber: this equipment is designed to reduce gaseous emissions. It includes a 556liter filling bath with a float and an emergency drain to handle the overflow. A soda solution is added for neutralization, and the liquid level must be checked before starting the plant. The optimal operating conditions require a pH range of 9-14. The fan and recirculation pumps are software-controlled, and if the scrubber fails to start, other operations will not begin.
- Chemical Reactor R101: it has a 200-litre capacity, is designed for solid-liquid extraction, it is constructed in steel but is acid-resistant thanks to its ebonite coating. It includes an agitator (M101) for mixing solutions and utilizes manual and automatic loading for solids, water, and chemicals. The reactor's discharge is controlled by a software-managed solenoid valve (VR101), and a weight cell displays the reactor's contents. For the discharge operations, a pneumatic diaphragm pump (PP101) allows the suspension to be transferred to the filtration systems: cartridge filtration (FC101) or filter press (FP101).
- Plate & Frame Filter FP101: this equipment separates liquids and solids from leaching treatment suspensions. The filter press operation, including the automatic start of the pump (PC112), is managed via the electrical cabinet QE1, with the number of plates adjusted based on the suspension's solid content.
- Copper Electrolytic Cell (CE101): used for the copper electrowinning process, this cell contains a 178-litre bath with copper cathodes and titanium-coated anodes. The current and voltage can be adjusted and monitored through the three-phase rectifier display QE3. The copper-rich solution is loaded and recirculated by specific pumps and controlled via software.
- Precious and other Strategic Metals Electrolytic Cell (CE102): this cell, with a 20-litre capacity, is utilized for gold, silver, and indium electrowinning. It features copper, graphite, or silver cathodes and titanium-coated anodes. Current and voltage adjustments are made through the three-phase rectifier display QE3. Solutions rich in metals to be recovered are loaded and recirculated by designated pumps, with the discharge controlled by software.





Each equipment plays a critical role in the plant's operation, with specific functions ranging from emission control to the extraction and separation of valuable metals. Proper operation, monitoring, and maintenance of these components are crucial for efficient and safe plant performance. For further information, it is necessary to follow the specific manuals for each equipment available at the plant.

The <u>control panel area</u> is located on the right side of the container, and it is composed of:

- Computer Workstation: the PLC software manages the control of scrubbers, automatic valves, and pumps. It includes registered recipes for hydrometallurgical processes used in the Treasure project to treat various materials from the automotive sector. You can also input different hydrometallurgical treatment procedures, along with quantities of chemicals, water, and solids. If the total volume exceeds the useful volume of the reactor, the software will prevent you from starting the treatment. During a test, a series of messages will appear on the screen indicating which valves to open or close during each operation.
- Electrical Cabinet: there is a main switch in the plant that is equipped with manual selector switches, allowing for the management of different equipment in manual or automatic mode.

The <u>chemical storage area</u> is located outside the plant and consists of six IBCs. These IBCs store the main chemicals used for hydrometallurgical treatments, including 50% sulfuric acid, 35% hydrogen peroxide, 80% acetic acid, and 32% hydrochloric acid. There are also two additional IBCs as reserves.

To transfer chemicals to reactors or other external tanks, each tank is equipped with a centrifugal pump (PC101-PC106) that is activated using software, ensuring that all valves along the pipes are open. Automatic valves (VP101A-VP106A) and (VP101B-VP106B) are installed on the suction and delivery pipes, with the latter allowing for flow rate adjustment. Additionally, an automatic valve is installed on each tank (VT101-VT106), and a manual valve (VL101-VL106) allows for the transfer of chemicals to other tanks outside the plant.

In Figure 2, the picture shows the connection of two IBC chemical storage tanks to the plant.



Figure 2. IBC chemical storage located outside the plant and automatically connected.





3. Starting phase of the plant

Below is a list of required steps to follow to start a test:

- 1. Check the pressure value at the pressure gauge (FR101) placed in the air inlet pipe (ordinary value 5-8 bar).
- 2. Check that the liquid level in the scrubber bath is correct. Verify that VA101, VA104, VA106, VB101, VB102, and VP112 are opened. Check the pH value of the liquid, which should be in the range of 9-14.
- 3. Turn on the main black switch located in the electrical cabinet of the control panel area (move from 0 to 1).
- 4. Switch on the computer and launch the dedicated software.
- 5. Login with username and password by clicking on SYS.
- 6. Check if errors appear on the screen; click on 'historical alarms'; if errors are solved, they can be deleted by clicking on 'reset alarm'.
- Click on 'scrubber,' and click on start VE101; when the icon becomes green, wait some seconds that the actual pressure reaches the reference pressure value (-40 mmH2O), and then click on start PC111; when it becomes green, the scrubber is correctly working.
- 8. The 'main' screen presents a general view of the plant; for instance, clicking on 'recipe' makes it possible to create a new test or utilize a pre-set test to start a cycle.
- 9. To create a new test, click on 'recipe' and insert in chronological order (1, 2, 3, 4....) the correspondent tank in which is present the chemical that you need. If you decide to exclude a tank insert 0. Then, insert the amount of each chemical, water, and solid. You can also set the time of reaction and the stirring speed.





4. Operational procedure for conducting hydrometallurgical processes

The following section provides a detailed description of the specific operations involved in carrying out hydrometallurgical processes. These operations have been tested and validated as part of the Treasure project. The procedures are programmed into the PLC software, which offers step-by-step guidance to the operator during the test run by issuing various alerts.

The procedures required to conduct the hydrometallurgical process for treating in-mold electronics, PCBs (powders and electronic components), and ITO glass of LCDs are outlined below.

4.1 Procedure for the treatment of in-mold electronics

The following are the necessary steps for carrying out the hydrometallurgical process to recover silver from different types of in-mold electronics.

Before starting, ensure that the actions mentioned in paragraph 3 have been positively completed.

The required amount of water and liquid chemicals can be selected by software. The time required for reactions between operations is also indicated by the software.

Preparing the leaching solution in the chemical reactor R102:

- 1. Water loading (opening VA101, VA201)
- 2. Loading thiourea powders manually.
- 3. Loading ferric sulphate powders manually.
- 4. Loading of sulfuric acid (opening valves VC201, VT101, VP101A, VP101B and starting the PC101 pump).
- 5. Mixing, the M102 impeller automatically starts and stops based on a set minimum quantity to guarantee the immersion of the blades.
- 6. Check the presence of the cartridge filters in FC201 and FC202.
- 7. Discharge of the solution from R102 into TK110 (opening valves VR201, VP201, VF201, VF202 and starting the PP201 pump).

Silver leaching in the chemical reactor R103:

- 1. Loading the solid in the chemical reactor R103 manually.
- Loading of the leaching solution from TK110 opening valves VT110B, VP108A, VP108B, VC307 and starting the PC108 pump the pump will automatically stop the valves as well close based on a quantity entered in the recipe.
- 3. The chemical reaction ends based on the time selected in the software.
- 4. Prepare the cartridge filter (5 μ m in nylon) in FC301.
- 5. Separate the leach liquor from the solid by using FC301. Discharge the filtered solution into TK111 (opening valves VR301, VP301, VF301, and VT111A, and start the pump PP301).
- 6. Stop the PP301 and close all the valves previously opened when all the solution has been discharged.
- 7. Washing of the solid. Water loading by opening valves VA101 and VA302.





- 8. Discharge the washing water into TK110 (can be reused for next leaching) by opening valves VR301, VP301, VF301, and VT110 A, then also start the pump PP301. When finished close the valves and stop the pump.
- 9. Opening the FC301 filter to recover some solid particles detached from the in-mold electronics samples.
- 10. Pull out the solid residue washed by the chemical reactor R103 manually by the side door.

Silver electrodeposition by using the electrolytic cell CE102:

- 1. Insert the silver cathode and the two titanium anodes inside the cell CE102.
- 2. Loading of the leach liquor solution from TK111 to the cell CE102 opening valves VT111B, VP108A, VP108B, VJ102, VH102 and start the pump PC108.
- 3. Charge the solution into the cell until the LSH102 indicator becomes orange, indicating the right level for electrodeposition. Then stop the pump, close the valves previously opened, and open the valve VP110C.
- 4. Switch on the rectifier and set the voltage to 1.3 V. The recirculating pump PC110 will start automatically. Allow 5 minutes for the power supply to initialize.
- 5. Once the 2-hour electrodeposition process is complete, the rectifier must be turned off.
- 6. Discharge the solution into the TK112 opening valves VP110A and VP110B and then start pump PC113.
- 7. When all the solution has been discharged, stop pump PC110, close valve VP110C, stop pump PC113, and close the valves VP110A and VP110B.
- 8. Manually recover the cathode with deposited silver powder and thoroughly clean the equipment.

4.2 Procedure for the treatment of printed circuit boards

The following are the necessary steps for carrying out the hydrometallurgical process to recover precious and base metals from different types of PCBs.

Before starting, ensure that the actions mentioned in paragraph 3 have been positively completed.

The required amount of water and liquid chemicals can be selected by software. The time required for reactions between operations is also indicated by the software.

Treatment of PCB powders

Base metals leaching (Cu and Sn) in the chemical reactor R102:

- 1. Water loading (opening VA101, VA201)
- 2. Loading of sulfuric acid (opening valves VC201, VT101, VP101A, VP101B and starting the PC101 pump).
- 3. Loading half of the amount of hydrogen peroxide by opening valves VC202, VT102, VP102A, and VP102B as well as starting the pump PC102.
- 4. Mixing, the M102 impeller automatically starts and stops based on a set minimum quantity to guarantee the immersion of the blades.
- 5. Manually load the PCB powders and verify the amount using control WIC102.
- 6. During the chemical reaction, repeat step 3 twice, adding one-quarter of the required amount of hydrogen peroxide each time.



- 7. Check the presence of the bag filter FC201.
- 8. Discharge of the leach liquor solution from R102 into TK107 (opening valves VR201, VP201, VF201, VF202 and VT107A and starting the PP201 pump). When the solution has been filtered close all the valves and stop the pump.
- 9. Washing with water (opening valve VA101, VA201) and discharge the washing water in another tank (TK108/TK109).
- 10. Recover the PCB powders/solid residue from the bag filter FC201.

Tin recovery by using the chemical reactor R102:

- 1. Loading of the leach liquor solution from TK107 to R102 (opening valves VT107B, VP107A, VP107B, VC208). Start pump PC107.
- 2. Mixing M102 automatically starts and stops based on a set minimum quantity to guarantee the immersion of the blades.
- 3. Prepare the polyamine dosage and add it manually into the chemical reactor R102.
- 4. After the time of reaction is ended prepare the cartridge filter FC202 (0.45 μm in nylon).
- 5. Start the filtration discharge the leach liquor solution from R102 into TK107 (opening valves VR201, VP201, VF201, VF202, and VT107A and starting the PP201 pump). When the solution has been filtered close all the valves and stop the pump.
- 6. Washing with water (opening valve VA101, VA201) and discharge the washing water in another tank (TK108/TK109).
- 7. Recover the powder of metastannic acid by opening the cartridge filter FC202.
- 8. The thermal treatment to obtain tin oxide is carried out in an external furnace.

Copper recovery by using the electrolytic cell CE101:

- 1. Insert the copper cathodes and the titanium anodes inside the cell CE101.
- 2. Loading of the leach liquor solution from TK107 to the cell CE101 opening valves VT107B, VP107A, VP107B, VJ101, VH101 and start the pump PC107.
- 3. Charge the solution into the cell until the LSH101 indicator becomes orange, indicating the right level for electrodeposition. Then stop the pump, close the valves previously opened, and open the valve VP109C.
- 4. Switch on the rectifier and set the voltage to 2.3 V. The recirculating pump PC109 will start automatically. Allow 5 minutes for the power supply to initialize.
- 5. Once the 1-hour electrodeposition process is complete, the rectifier must be turned off.
- 6. Discharge the solution into the TK109 opening valves VP109D, VP109A, VP109B and then start pump PC112.
- 7. When all the solution has been discharged, stop pump PC109, close valve VP109C, stop pump PC112, and close the valves VP109D, VP109A and VP109B.
- 8. Manually recover the cathode with deposited copper powder and thoroughly clean the equipment.

Precious metals leaching (Au and Ag) in the chemical reactor R102:

- 1. Water loading (opening VA101, VA201)
- 2. Loading thiourea powders manually.
- 3. Loading ferric sulphate powders manually.





- 4. Loading of sulfuric acid (opening valves VC201, VT101, VP101A, VP101B and starting the PC101 pump).
- 5. Mixing, the M102 impeller automatically starts and stops based on a set minimum quantity to guarantee the immersion of the blades.
- 6. Manually loading the solid residue powder obtained by the base metals leaching operation.
- 7. After 1 hour of reaction, prepare for the filtration.
- 8. Check the presence of the bag filter FC201.
- Discharge of the leach liquor solution from R102 into TK110 (opening valves VR201, VP201, VF201, VF202 and VT110A and starting the PP201 pump). When the solution has been filtered close all the valves and stop the pump.
- 10. Washing with water (opening valve VA101, VA201) and discharge the washing water in TK111 by opening valves TK111A and the pump PP201.
- 11. Recover the PCB powders/solid residue from the bag filter FC201.

Gold-silver recovery by using the electrolytic cell CE102:

- 1. Insert the graphite cathode and the two titanium anodes inside the cell CE102.
- Loading of the leach liquor solution from TK111 to the cell CE102 opening valves VT111B, VP108A, VP108B, VJ102, VH102 and start the pump PC108.
- 3. Charge the solution into the cell until the LSH102 indicator becomes orange, indicating the right level for electrodeposition. Then stop the pump, close the valves previously opened, and open the valve VP110C.
- 4. Switch on the rectifier and set the voltage to 1.5V. The recirculating pump PC110 will start automatically. Allow 5 minutes for the power supply to initialize.
- 5. Once the 2-hour electrodeposition process is complete, the rectifier must be turned off.
- 6. Discharge the solution into the TK112 opening valves VP110A and VP110B and then start pump PC113.
- 7. When all the solution has been discharged, stop pump PC110, close valve VP110C, stop pump PC113, and close the valves VP110A and VP110B.
- 8. Manually recover the cathode with deposited gold-silver (dorè) powder and thoroughly clean the equipment.
- 9. The refining of silver and gold must be conducted in the plant's quality laboratory and service control. The operations include nitric acid leaching, precipitation of silver chloride by adding sodium carbonate, and refining of gold in a furnace at 1065°C.

Treatment of electronic components

Base and precious metals leaching in the chemical reactor R103:

- 1. Loading the solid in the chemical reactor R103 manually.
- 2. Loading of the water (opening valves VA101 and VA301).
- 3. Loading of acetic acid (opening valves VC306, VT106, VP106A, VP106B and starting the PC106 pump).
- Loading of hydrochloric acid half of the required amount (opening valves VC305, VT105, VP105A, VP105B and starting the PC105 pump).
- Loading of hydrogen peroxide half of the required amount (opening valves VC302, VT102, VP102A, VP102B and starting the PC102 pump).





- 6. Loading of hydrochloric acid 25% of the necessary amount (opening valves VC305, VT105, VP105A, VP105B and starting the PC105 pump).
- Loading of hydrogen peroxide 25% of the necessary amount (opening valves VC302, VT102, VP102A, VP102B and starting the PC102 pump).
- Loading of hydrochloric acid 25% of the necessary amount (opening valves VC305, VT105, VP105A, VP105B and starting the PC105 pump).
- 9. Loading of hydrogen peroxide 25% of the necessary amount (opening valves VC302, VT102, VP102A, VP102B and starting the PC102 pump).
- 10. The chemical reaction ends based on the time selected in the software.
- 11. Prepare the cartridge filter (5 μ m in nylon) in FC301.
- 12. Separate the leach liquor from the solid by using FC301. Discharge the filtered solution into TK111 (opening valves VR301, VP301, VF301, and VT111A, and start the pump PP301).
- 13. Stop the PP301 and close all the valves previously opened when all the solution has been discharged.
- 14. Washing of the solid. Water loading by opening valves VA101 and VA302.
- 15. Discharge the washing water into TK110 (can be reused for next leaching) by opening valves VR301, VP301, VF301, and VT110 A, then also start the pump PP301. When finished close the valves and stop the pump.
- 16. Opening the FC301 filter to recover some solid particles detached from the electronic components.
- 17. Pull out the solid residue washed by the chemical reactor R103 manually by the side door.

Gold recovery by adding ascorbic acid in chemical reactor R102:

- 1. Loading of the leach liquor solution from TK111 to R102 (opening valves VT111B, VP108A, VP108B, VC207). Start pump PC108.
- 2. Mixing M102 automatically starts and stops based on a set minimum quantity to guarantee the immersion of the blades.
- 3. Load the required amount of ascorbic acid manually into the chemical reactor R102 and add it slowly.
- 4. After the time of reaction is ended prepare the cartridge filter FC202 (0.45 μm in ceramic).
- 5. Start the filtration discharge the leach liquor solution from R102 into TK111 (opening valves VR201, VP201, VF201, VF202, and VT111A and starting the PP201 pump). When the solution has been filtered close all the valves and stop the pump.
- 6. Washing with water (opening valve VA101, VA201) and discharge the washing water in another tank (TK110).
- 7. Recover the powder of gold-ascorbate by opening the cartridge filter FC202.
- 8. The thermal treatment to obtain refined gold metal is carried out in an external furnace.

Silver recovery by lowering the temperature in chemical reactor R102:

- 1. Loading of the leach liquor solution from TK111 to R102 (opening valves VT111B, VP108A, VP108B, VC207). Start pump PC108.
- 2. Mixing M102 automatically starts and stops based on a set minimum quantity to guarantee the immersion of the blades.





- 3. Switch on the chiller and manually open the valves for the recirculation of cold water in the coil of chemical reactor R102. Start the external pump for water recirculation.
- 4. Check when the temperature decreases to 5°C by the TIC102 control. This is the start time of the reaction.
- 5. After the time of reaction is ended prepare the cartridge filter FC202 (0.45 μm in ceramic).
- 6. Start the filtration discharge the leach liquor solution from R102 into TK111 (opening valves VR201, VP201, VF201, VF202, and VT111A and starting the PP201 pump). When the solution has been filtered close all the valves and stop the pump.
- 7. Washing with water (opening valve VA101, VA201) and discharge the washing water in another tank (TK110).
- 8. Recover the powder of silver chloride by opening the cartridge filter FC202.

Chemical cementation of palladium/copper/tin into the chemical reactor R102:

- 1. Loading of the leach liquor solution from TK111 to R102 (opening valves VT111B, VP108A, VP108B, VC207). Start pump PC108.
- 2. Mixing M102 automatically starts and stops based on a set minimum quantity to guarantee the immersion of the blades.
- 3. Prepare the required amount of copper/tin/zinc metallic powder and add it manually into the chemical reactor R102.
- 4. After the time of reaction is ended prepare the cartridge filter FC202 (5 μ m in nylon).
- 5. Start the filtration discharge the leach liquor solution from R102 into TK111 (opening valves VR201, VP201, VF201, VF202, and VT111A and starting the PP201 pump). When the solution has been filtered close all the valves and stop the pump.
- 6. Washing with water (opening valve VA101, VA201) and discharge the washing water in another tank (TK110).
- 7. Recover the powder of palladium/copper/tin by opening the cartridge filter FC202.

4.3 Procedure for the treatment of ITO glass of LCDs

The following are the necessary steps for carrying out the hydrometallurgical process to recover indium from the ITO glass of LCDs.

Before starting, ensure that the actions mentioned in paragraph 3 have been positively completed.

The required amount of water and liquid chemicals can be selected by software. The time required for reactions between operations is also indicated by the software.

Preparing the leaching solution in the chemical reactor R102:

- 1. Water loading (opening VA101, VA201)
- 2. Loading of sulfuric acid (opening valves VC201, VT101, VP101A, VP101B and starting the PC101 pump).
- 3. Mixing, the M102 impeller automatically starts and stops based on a set minimum quantity to guarantee the immersion of the blades.
- 4. Check the presence of the cartridge filters in FC201 and FC202.





5. Discharge of the solution from R102 into TK110 (opening valves VR201, VP201, VF201, VF202 and starting the PP201 pump).

Indium leaching in the chemical reactor R103:

- 1. Loading the solid in the chemical reactor R103 manually.
- 2. Switch on the boiler and open the valves for the recirculation of hot water in the coil. Start the external pump for water recirculation.
- 3. Check when the temperature reaches 60°C with the TIC103 control. At this point proceed to the next step.
- 4. Loading of the leaching solution from TK110 opening valves VT110B, VP108A, VP108B, VC307 and starting the PC108 pump – the pump will automatically stop the valves as well close based on a quantity entered in the recipe.
- 5. The chemical reaction ends based on the time selected in the software.
- 6. Prepare the cartridge filter (5 μm in nylon) in FC301.
- 7. Separate the leach liquor from the solid by using FC301. Discharge the filtered solution into TK111 (opening valves VR301, VP301, VF301, and VT111A, and start the pump PP301).
- 8. Stop the PP301 and close all the valves previously opened when all the solution has been discharged.
- 9. Washing of the solid. Water loading by opening valves VA101 and VA302.
- 10. Discharge the washing water into TK110 (can be reused for next leaching) by opening valves VR301, VP301, VF301, and VT110A, then also start the pump PP301. When finished close the valves and stop the pump.
- 11. Opening the FC301 filter to recover some solid particles detached from the ITO glass samples.
- 12. Pull out the solid residue/glass washed by the chemical reactor R103 manually by the side door.

Indium electrodeposition by using the electrolytic cell CE102:

- 1. Insert the graphite cathode and the two titanium anodes inside the cell CE102.
- 2. Loading of the leach liquor solution from TK111 to the cell CE102 opening valves VT111B, VP108A, VP108B, VJ102, VH102 and start the pump PC108.
- 3. Charge the solution into the cell until the LSH102 indicator becomes orange, indicating the right level for electrodeposition. Then stop the pump, close the valves previously opened, and open the valve VP110C.
- 4. Switch on the rectifier and set the voltage to 2.5 V. The recirculating pump PC110 will start automatically. Allow 5 minutes for the power supply to initialize.
- 5. Once the 2-hour electrodeposition process is complete, the rectifier must be turned off.
- 6. Discharge the solution into the TK112 opening valves VP110A and VP110B and then start pump PC113.
- 7. When all the solution has been discharged, stop pump PC110, close valve VP110C, stop pump PC113, and close the valves VP110A and VP110B.
- 8. Manually recover the cathode with deposited indium powder and thoroughly clean the equipment.





5. Maintenance and safety practices

In this section, a series of maintenance operations and good security practices are reported.

- Always use personal protective equipment (PPE): acid-resistant gloves, air-purifying respirator, lab coat, glasses, and safety shoes.
- Before starting any operations, check the pressure on the pressure gauge (FR101) and, if necessary, turn on the air compressor, check the solution level of the scrubber bath, and remember to add soda sometimes to neutralize acid gases.
- Check for leaks from the pipes and eventually dry them to avoid corrosion. Solve the problems that caused the dripping.
- Once the solutions have been discharged from all the equipment utilized, they must be washed with water to remove all residual deposits and dried.
- During the loading of the reactor, if you are working in manual mode, take care not to exceed the useful volume of the reactor. Instead, in the case of automatic mode, it will be the software that signals it and prevents the loading.
- During the loading of solid in the reactor, be careful to avoid splashing and always check the correct particle size of the solid. If the particle size is above 2 mm, the pipes can be blocked. In this case, we can try to help the flow by blowing compressed air; otherwise, it is necessary to dismantle the pump PP101 or the nearby pipes. Anyway, periodically check if there is a residual material in pump PP101.
- Before starting the filtration operation, check that all the plates are inserted; otherwise, the closing cycle doesn't work. Check also if the plates are correctly placed as a function of the pipes.
- Before starting the electrodeposition check that cathodes and anodes make contact with the copper bars.
- During the electrodeposition, check for leaks from the extractor hood, and eventually dry it.
- Check that the rectifier temperature does not exceed 60 degrees. Otherwise, excessive overheating will stop the treatment.
- Check the timer of rectifiers; if they are set, the electrowinning will be interrupted. Disable the timer if the time of reaction is not known.





Abbreviations

IBC	Intermediate Bulk Container
ІТО	Indium-Tin Oxide
LCDs	Liquid Crystal Displays
РСВ	Printed Circuit Board
PLC	Programmable Logic Controller
SME	Small Medium Enterprise
WEEE	Waste from Electrical and Electronic Equipment





References

[1] Directive 2006/42/EC of the European Parliament and of the Council of 17 May 2006 on machinery, and amending Directive 95/16/EC.




D6.2: Report on biohydrometallurgical materials recovery

<u>Annex 2 – Materials recycling</u> <u>recovery assessment report (updated</u> <u>version)</u>

31/05/2024 (M36)

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1. Introduction

The purpose of this ANNEX is to present an updated analysis of the recycling performance for processing various car electronics. This will involve comparing a wide simulation of existing metallurgical recycling processes investigated by MARAS with the bio-hydrometallurgical processes validated on a pilot scale by UNIVAQ that have been tested experimentally on materials provided by project partners such as TNO, ILSSA, SEAT, POLLINI and EUROLCDs.

In D5.5, a comprehensive study was conducted to compare existing metallurgical processes with bio-hydrometallurgical processes with the results of the experiments carried out on a laboratory scale by UNIVAQ (D5.4), which identified the need for some optimizations. Based on the outcomes described by UNIVAQ in D6.2 on the pilot plant tests, the results of bio-hydrometallurgical processes have been refined, particularly concerning mass balances, recovery rates of various metals, and the purity achieved in the final products.

2. Comparison of recycling process options

The comparison between the simulation of existing metallurgical processes and the processes developed by UNIVAQ and validated on a pilot scale within the TREASURE project was conducted on the following materials:

- In-mold electronics (provided by TNO)
- Printed circuit boards from car dashboards (provided by ILSSA, POLLINI and SEAT)

Due to the fact that full compositional data of the materials are required for the simulation, and the data on just elemental composition are not sufficient, this comparison was not made for the treatment of ITO glass by LCDs and for some specific gold-plated electronic components for which UNIVAQ has identified and developed a specific hydrometallurgical treatment.

2.1 Recycling of In-mold electronics

Table 1 compares the recovery rates of different metals potentially achievable through existing metallurgical processes with those achieved through the bio-hydrometallurgical process developed by UNIVAQ and tested on the pilot plant. It must be said that UNIVAQ focuses on the recovery of only some specific metals based on their intrinsic economic value. In the case of inmold electronics, UNIVAQ has focused exclusively on silver recovery, contributing to almost 98% of the total intrinsic economic value (more details are explained in D6.4).

Elements/metals/compounds	Recycling in existing processing options	Recycling in UNIVAQ bio- hydrometallurgical pilot plant
	Recovery %	Recovery %
Ag	98.42	82.9
Si	99.00 (as SiO ₂ in slag)	*
Са	99.00 – recovered in slag as CaO	*
Cu	99.06	*
Plastics (PC)	recovered as energy and reductant	investigated by TNO after the bio-hydrometallurgical process (80% of polycarbonate recycling)
Р	100	*
Pb (in bullion)	96.46	*
TiO ₂	100	*

Table 1 Possible recycling rates for the recycling of IME as achieved by existing processing and achieved recycling rates from UNIVAQ by testing bio-hydrometallurgical processes at a pilot scale.

*Not investigated, given the low intrinsic economic value

We have observed that existing metallurgical processes can recover all the elements from inmold electronics, including Ag, Si, Ca, Cu, P, Pb, and Ti, with high recovery rates. The biohydrometallurgical process developed by UNIVAQ specifically focuses on silver recovery and has achieved a total recovery rate of 82.9%. Although hydrometallurgical technologies have shown the potential to achieve yields higher than 95% in laboratory scale tests conducted by UNIVAQ (D5.4), a decision was made to develop a process that requires less water and reagents, involving only two acid leaching stages. UNIVAQ's approach aims to identify the optimal conditions to maximize the recovery of the material's economic value while minimizing wastewater production, one of the most significant limitations of hydrometallurgical processes. Comparing the recovery of silver between the two processes shows how 98.4% of Ag can be recovered through existing metallurgical processes compared to 82.9% in the hydrometallurgical process developed by UNIVAQ and experimentally tested at a pilot scale.

Table 2, however, displays the achievable purity of silver and copper for existing metallurgical processes and the purity of silver achieved by the pilot-scale UNIVAQ bio-hydrometallurgical process.

Table 2 Purity of recovered metals for the recycling of IME as achieved by existing processing
and by the UNIVAQ bio-hydrometallurgical processes tested at pilot scale.

Recovered metals	Existing processing options Purity %	UNIVAQ bio-hydrometallurgical process (pilot scale) Purity %
Ag	99.999 (electrolytic)	98.57
Cu	99.999 (electrolytic)	*

*Not investigated, given the low intrinsic economic value

As for the products obtained from the recycling process, the existing metallurgical processes can obtain 99.999% grade, while UNIVAQ, through experimentation on a pilot scale of the developed hydrometallurgical process, has achieved a purity of 98.57% through a recovery of silver from the leach liquor solution by electrodeposition. Possible increases in purity should be investigated on an industrial scale by introducing dedicated thermal refining treatments. It should be considered that the hydrometallurgical pilot plant reconfigured as part of the Treasure project is an experimental plant suitable for testing and validating the recycling of different types of materials in the automotive sector. If an industrial plant is built, it is clear that it would be necessary to select more specific equipment to improve both the recovery and purity of the metals.

Based on the current comparison, the UNIVAQ process has produced encouraging results, considering the improvements seen during the scale-up from laboratory to pilot scale. Anyway, existing metallurgical processes based on conducted simulations allow for a higher recovery and purity and recovery of additional elements.

Table 3 presents the products that can be obtained and the energy recovery from the recycling process of in-mold electronics. The process was simulated and carried out on a larger scale (20 tph).

Table 3 Products from IME recycling processing in energy recovery processing (note that the processing has been simulated and is performed at a larger scale of 20 tph)

Mass balance/products from IME recycling in energy recovery processing per 1000 kg of IMSE feed	Composition	Amount	Unit
Total part feed tph		100	kg
Metal phase (recycled to other units in flowsheet)	98.2 % Cu and 1.8% Ag	0.5	kg
Flue dust phase (recycled to other units in flowsheet)	Ag ₂ O	0.21	kg

Energy (if 100% efficient boiler)	52.9 % N ₂ ; 3.0 % CO ₂ ; 4.6% H ₂ O; 20.7% CO; 18.7% H ₂ and rest	4798.26	kW
Energy recovery per tonne of feed		0.24	MWh/t
Calcine (to recovery process of TiO_2 and P)	98.8% TiO ₂ , 1.2% P ₂ O ₅	85.5	kg

The major products of recycling the IME in this flowsheet configuration of processes are:

- Energy (see Table 3)
- Metal alloy/phase due to reducing gases: ca. 98.2 % Cu and ca. 1.8% Ag, which is recycled to the reductive (Cu) smelter (see Figures 3&4).
- Flue dust: Essentially pure Ag₂O, which is recycled to the reductive (Cu) smelter (see Figure 4).
- Synthesis gas if not oxidized for energy recovery (ca. 52.9 % N₂; 3% CO₂; 4.6% H₂O; 20.7% CO; 18.7% H₂ and rest, which can be used as fuel or reductant).
- Calcine, which is basically pure, i.e., ca. 98.8% TiO₂ and the rest P₂O₅. This can be recycled for TiO₂ and P recovery (Table 3 below).

Table 4 shows the material balance of the bio-hydrometallurgical process (UNIVAQ) for the recycling of in-mold electronics based on the results obtained on a pilot scale.

Table 4 Mass balance for the bio-hydrometallurgica	al process (UNIVAQ) per 1 ton of IME,	pilot
scale.		

Input, kg		Output, kg		
solid (IME)	1000.0	dry solid/secondary product	984.0	
water	464.3	humidity	47.1	
thiourea	130.7	silver powder	7.7	
ferric sulphate	449.6	treated water to sewerage	1189.3	
sulfuric acid, 50 %	131.5	wet sludges	666.7	
hydrogen peroxide, 30%	571.7	-	-	
lime, 10%	147.2	-	-	
	2894.8		2894.8	

The use of fresh water is 464.3 kg per ton of in-mold electronics, which is significantly lower than generally used in hydrometallurgical processes [1]. Hydrometallurgical processes always include a leaching stage to dissolve metals from the solid. Such an operation is usually conducted at a solid concentration in the range of 10-20 wt. %, which would imply that to treat a ton of solid (in-mold electronics in this case) would require 5-10 tons of water. This is only valid if there is only one leaching stage; in other cases, these amounts of water would be multiplied by the number of stages required by the process. Therefore, the result achieved by UNIVAQ in terms of freshwater consumption is very important to position this process relative to other hydrometallurgical processes. This result has been possible thanks to adopting techniques that allow solutions to be reused and introducing a wastewater treatment section.

Regarding chemical reagents, 50 % sulphuric acid (131.5 kg per ton of processed IME) and thiourea (130.7 kg per ton processed IME) have been reduced by exploiting a partial regeneration that occurs during electrodeposition. The consumption of ferric sulfate (449.6 kg

per ton of IME processed) is higher since it is completely consumed during each leaching. Hydrogen peroxide and lime use occur in the wastewater treatment section, allowing for zero liquid discharge production.

The products obtained by the bio-hydrometallurgical process are listed below:

- Silver powder.
- Treated water with quality characteristics suitable for reuse in the plant as service water and that does not need further treatment.
- Dry solid residue, this is one of the most critical aspects that needs more investigation although TNO has observed through specific analysis that the solid residue essentially made of polycarbonate has seen a reduction in molecular weight light and so the hydrometallurgical technique does not prevent a subsequent recovery of polycarbonate.
- Wet sludge that needs to be properly disposed of.
- Humidity.

2.2 Recycling of PCBs

Regarding the recycling of PCBs, it was not possible to compare the recycling of the same materials due to the lack of compositional data needed to evaluate the efficiencies that existing metallurgical processes can achieve, although the overall composition is expected to be comparable.

To assess the recyclability of the PCBs, MARAS used full compositional data provided by SEAT for two types of PCBs from the SEAT LEON II model, called PCB type 1 and PCB type 2.

About the process developed by UNIVAQ for the recycling of PCBs, two specific hydrometallurgical routes have been identified through a preliminary disassembly operation to remove some specific electronic components. The board with some residual components is grinded, and powders are obtained, which are then subjected to a process that has been developed starting from the Gold-REC1 patent. Gold-plated electronic components removed in advance undergo another specific hydrometallurgical process developed starting from the Gold-REC1 patent.

Table 5 shows the updated comparison in terms of recovery rates for the two processes investigated by MARAS and the two hydrometallurgical processes based on the pilot scale tests conducted by UNIVAQ.

Elements/metals/compounds of different types of PCB	Existing processing – Cu recycling infrastructure		UNIVAQ bio-hydrometallurgical process (pilot scale/prototypal plant)	
	PCB type 1 % Recovery	PCB type 2 % Recovery	GDR1 % Recovery	GDR2 % Recovery
Ag (99.999% purity electrolytic)	98.8	95.8	67.7	72.8
Al, Ba, Ca, Fe, Mg, Si (as Al ₂ O ₃ , BaO, CaO, FeOx, SiO ₂ in slag)	99.0	99.0	not investigated	not investigated
Au	99.0	99.0	78.9	93.7

Table 5 Results of recycling rates processing of different PCB types in the Cu processing route and two UNIVAQ processes (GDR1 and GDR2)

Cu (99.999% purity) electrolytic	98.0	99.0	97.3	88.4
In (to alloy for further processing)	3.12	0.00	not investigated	not investigated
Sn (to various intermediates for further processing to recover rest)	74.8	78.0	91.6	76.0
Zn (99.99+% electrolytic)	62.4	33.9	not investigated	not investigated
Pb	95.7	96.1	not investigated	not investigated
Pd	100.0	100.0	*	38.0
Pt	99.9	Not present in feed	not investigated	not investigated
Plastics / organics	recovered as energy and reductant	recovered as energy and reductant	not investigated	not investigated
Ni (99.99+% electrolytic)	96.6	96.1	not investigated	not investigated
Co (99.99+% electrolytic)	93.1	92.6	not investigated	not investigated

*Pd can't be recovered since is present in low concentration in the feed

In this case, it can also be observed how, through the existing metallurgical processes, it is possible to recover more elements with higher recovery rates than the hydrometallurgical processes. As for palladium, the low recovery value obtainable with the GDR2 process depends on the fact that the concentration in the initial material is very low; if the concentration is higher, it would be possible to obtain higher recovery rates.

It's crucial to highlight that the approach of UNIVAQ is completely different. The focus is on developing processes to recover certain specific metals with a higher economic value from a product, ensuring the possibility of generating a profit. Based on specific needs, hydrometallurgical technologies could still be suitable for selective recovery of other metals; however, a preliminary cost-benefit analysis must be conducted to evaluate the economic feasibility.

Table 6 shows the comparison of the purity achievable for the recovered products.

Table 6 Purity of recovered materials for the recycling of different PCB types in the Cuprocessing route and in two UNIVAQ processes (GDR1 and GDR2)

Recovered	Existing processing	UNIVAQ bio-hydrometallurgical processes (pilot scale/prototype plant)	
metals	options	GDR1 (pilot scale)	GDR2 (prototype plant)
	Purity %	Purity %	Purity %
Ag	99.999	99.8 as chloride	95.0 as chloride
Au	99.999	99.1	99.2

Pd		not present in the material	84.9
Cu	99.999	99.4	92.3
Sn	to various intermediates for further processing to recover Sn	99.1 as oxide	96.1
Zn	99.999	Not investigated	Not investigated
Ni	99.999	Not investigated	Not investigated
Со	99.999	Not investigated	Not investigated

In this case, the purities of the final products attainable through hydrometallurgical processes are always higher than 99% for the GDR1 process. In the case of GDR2, the gold purity exceeds 99%, while the other purities are lower due to contamination from the metal used for chemical cementation. Further improvements could be achieved through thermal refinements, which need to be investigated in higher amounts at an industrial level. The purity potentially achievable through existing metallurgical processes is even higher, reaching up to 99.999%.

Table 7 shows the mass balance for the two metallurgical processes investigated by MARAS from the SEAT LEON II PCBs. It shows that from the total input (with individual rates as given in Table 5), depending on the PCB type, around 50% can be recovered as valuable materials and that the plastics and organics are recovered as energy (and reductant) in this processing route. Hence, no residue of this input material is created. Metal, slag, and flue dust as created through this process can be applied either as closed-loop CE recycling products (metal phase) or as open-loop CE – (intermediate) products for repurposing e.g., as building/construction material, etc., rendering this type of processing effective in the realization of CE and recovery of materials and contained energy while minimizing the amount of input needed and residues and emissions created.

Products from PCB processing in Cu processing route (per ton of PCB)	PCB type 1 Amount	PCB type 2 Amount	Unit
Copper Alloy (Oxidative melting)	477	436.5	kg
Energy (if 30% efficient) Ox (recovered)	0	118.42	kW
Energy (if 30% efficient) Red (recovered)	8.79	8.19	kW
Energy recovered per tonne of feed (summarised Ox+Red)	8.79	126.61	kWh/t
Slag (building material)	34	29.5	kg
Total recovery of materials from input into valuable products	52.3%	48.5%	%

Table 7. Products from 1 ton PCB input recycling processing in Cu recycling route

Table 8 shows the mass balance obtained by pilot scale for the hydrometallurgical process GDR1 for the treatment of the powders of PCBs (tested on material supplied by ILSSA).

It's worth noting that with respect to D5.5 this process was significantly improved in terms of reduction of freshwater and chemical consumptions thanks to the reuses of solutions and to the introduction of dedicated wastewater treatment sections that allowed to do not have wastewater production. Specifically, freshwater consumption decreased by over 85% (1674 kg

of this scenario compared to 12045 kg of the previous scenario reported in D5.5). Another important aspect of this process is that it doesn't generate wastewater, as it is sent to specific sections and purified for reuse within the plant. The only wastewater generated is from gold and silver refining treatment, which is very low - only 2.7 kg per ton of processed PCB powders. This process allows the recovery of 0.075 kg of gold, 0.245 kg of silver chloride, 11.85 kg of tin oxide, and about 187 kg of copper from treating one ton of PCB powders. The purity of the obtained products is shown in the next tables. All other outputs, including their characterization, are given below.

Input	kg	Output	kg		
Solid	1000.0	Dry solid residue	781.0		
H ₂ SO ₄ (50 % w/v)	767.1	Treated water 1	2194.8		
H ₂ O ₂ (30 % w/v)	1771.2	Treated water 2	1736.4		
Thiourea	40.7	Wet sludge 1	255.7		
Ferric sulphate	181.9	Wet sludge 2	364.1		
Polyamine (10 % w/v)	19.1	Tin oxide	11.85		
Water for 1 st leaching stage	281.5	Copper 1	187.0		
Water for 2 nd leaching stage	1390.1	Gold	0.075		
Water for Au-Ag refining	2.4	Silver chloride	0.245		
Iron metallic powder	0.7	Humidity	755.3		
HNO₃ (65 % w/v)	0.2	Copper 2 from the WW section	0.7		
NaCl	0.1	Wastewater from the refining	2.7		
Lime (10% w/v)	1054.3				
Ferrous sulphate	13.2				
Total input	6522.5	Total output	6289.9		
Experimental error 3.6%					

Table 8 Mass balances for treating 1 ton of PCBs powders (GDR1 process), tested at pilot scale.

Table 9 shows the mass balance of the GDR2 process for the specific treatment of some electronic components, especially the gold-plated ones, that have been previously removed from the board. It has been described based on the outcomes of the prototypal tests for the hydrometallurgical section and based on the lab test for the evaporation section.

Table 9 Mass balances for the treatment of 1 ton of mixed gold-plated components in the UNIVAQ GDR2 process, tested at the prototype plant.

Input	kg	Output	kg
Solid	1000.0	Dry solid residue	641.0
HCl (32 % w/v)	1257.1	Gold	0.239
H ₂ O ₂ (30 % w/v)	1480.0	Silver chloride	0.584
C ₂ H ₄ O ₂ (80% w/v)	890.8	Palladium	0.0125

Water	390.6	Copper	172.1		
Ascorbic acid	33.3	Tin	17.1		
Copper metallic powder	40.0	HCl (1% w/v)	2857.0		
Tin metallic powder	186.7	Sludge	1237.0		
Zinc metallic powder	6.7	Humidity	185.2		
Total input	5285.1	Total output	5110.2		
Experimental error 3.3%					

The implementation of the evaporation section has resulted in a significant reduction in freshwater and hydrochloric acid consumption through solution reuse. Specifically, the freshwater consumption is 390.6 kg per ton of electronic components to be processed. Each ton of processed material yields the following outputs: 239 g of gold, 584 g of silver chloride, 12.5 g of palladium, 172 kg of copper, and 17 kg of tin. The only output that needs to be properly disposed of is the sludge, which is mainly composed of zinc chloride.

3. Conclusions

The comparison between existing metallurgical processes and bio-hydrometallurgical processes developed by UNIVAQ and tested on a pilot scale, for the recovery of strategic metals from automotive PCBs and in-mold electronics, has revealed the following results:

- Existing metallurgical processes can recover a larger number of metals with high recovery rates and purity almost always of 99.999%, as well as having an energy recovery from polymeric/organic materials.
- Bio-hydrometallurgical processes focus on the specific recovery of certain strategic metals that contribute most to the intrinsic economic value; the recoveries and the pureness obtained are promising, given the remarkable increase that has been had with the scale-up from laboratory to pilot plant.
- Bio-hydrometallurgical processes have been developed to include specific wastewater treatment and reagent recovery sections. These operations aimed to significantly overcome the typical challenges of hydrometallurgical processes regarding water usage. UNIVAQ processes adopted techniques such as counter-current leaching and reuse of solutions, which greatly reduce freshwater consumption. Although it's challenging to find references due to the confidentiality of mass balances in industrial-scale hydrometallurgical processes, scientific articles have confirmed that UNIVAQ processes consume significantly less water.

References

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