D5.4: Pilot-scale reconfiguration, testing and optimization of a materials recovery process

31/05/2023 (M24)

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EXECUTIVE SUMMARY

The TREASURE project aims to offer an opportunity to make the automotive sector more circular. This objective is pursued with the realization of tools that support the development of a circular supply chain with the possibility of testing different technologies. As already identified in the precursor FENIX project, the Key Enabling Technologies (KETs) can be integrated into various processes to obtain real benefits and to improve the efficient recovery of secondary resources.

The focus of D5.4, given the decision to reuse the existing FENIX hydrometallurgical pilot plant, is to carry out an overall reconfiguration to practical demonstrate innovative automotive supply chains. The pilot plant was reconfigured according to the TREASURE requirements. The present deliverable has also described the studies related to an optimization of the hydrometallurgical recycling processes developed in the ambit of the TREASURE materials by continuing in Task 5.4 the activities of Task 5.3.

D5.4 is composed of four annexes. The first is on the pilot scale reconfiguration activities, while the other annexes are on the recycling process optimization for different materials from the automotive sector.

In ANNEX 1, it is first described the pre-existent hydrometallurgical pilot plant. Then, the main objectives to be achieved are explained; they are related to the critical issues resulting from previous experience in the use of the pilot plant, to make the plant suitable for the treatment of TREASURE materials, and to automate it so that it can be completely governed by the PLC software. All the added equipment to achieve these objectives is fully described by explaining their specific added value. Then, the process and instrument diagram (P&ID) (ANNEX 1A), overall plant layout, and all detailed engineering documents will be produced during this phase. In the end, some pictures of the start-up test aimed at checking the correct working of all the equipment of the reconfigured pilot plant are shown.

ANNEX 2, ANNEX 3, and ANNEX 4 are related to the optimization of the recycling processes on in-mold structural electronics, liquid crystal displays, and printed circuit boards, respectively. A detailed characterization of the materials to be recycled using different analytical techniques is reported for each ANNEX. Then, hydrometallurgical optimization studies were described; the main aim was to increase the recoveries of the base, critical and precious metals by reducing the chemical consumption and the production of wastewater according to an MLD approach. Each output of the optimized process was characterized to understand how to manage them and to define the main elements' flow material. Balance materials, flowsheets' process, and economic and environmental evaluations were conducted.

TABLE OF CONTENTS

1. Pilot-scale reconfiguration

The reconfiguration of the hydrometallurgical pilot plant, built under a previous European project – H2020 FENIX, grant agreement No. 760792, was carried out. The main aim of FENIX was the development of new business models and industrial strategies for different novel supply chains to enable value-added product-services. To this aim, the hydrometallurgical pilot plant had the objective to produce 3D printing metal powders through the treatment of WEEE. This way, secondary raw materials could be obtained using a circular economy approach.

The pre-existent mobile pilot plant was realized in a 40 feet container. It was intended for the treatment of ground electronic board powders with a maximum size of 2 mm.

A detailed study was done to identify the pilot plant's possible implementations, starting from some critical issues shown during the experimental activities carried out as part of the FENIX project. One of the scopes of the reconfiguration was to modify and implement the plant in order that can process the materials of interest in the TREASURE project. More generally, the aim was also to make the plant more flexible for the treatment of different types of materials, not only powders. Therefore, more chemical reactors and filtration systems with different characteristics compared to those already present were added. Finally, all the valves were automated according to Industry 4.0.

The company engaged in carrying out the pilot plant reconfiguration was B.F.C. Sistemi S.r.l., the same company that built the plant in June 2019, so it was selected for economic and logical reasons.

Moreover, after the pilot plant's reconfiguration, start-up tests with water and a powder of printed circuit boards were done to check the equipment’s correct working.

The full details are reported in **ANNEX 1,** and the P&ID of the reconfigured hydrometallurgical pilot plant is shown in **ANNEX 1A**.

2. Recycling process optimization of in-mold structural electronics

The optimization of the hydrometallurgical process for the recycling of silver from IMSE samples, whereby silver is directly exposed on the surface, was performed. Moreover, a detailed characterization of the input and all the process outputs has been performed using different analytical techniques such as ICP-OES, XRD, FTIR, and XRF. The characterization and the hydrometallurgical process were investigated on different types of IMSEs like thermoformed, full silver area, elongated, and a mixture of all the samples provided by TNO Holst Centre. In addition, the characterization was also performed on different SMDs located on the surface of some samples. Based on the hydrometallurgical process optimization results, process analysis was made to propose a silver recycling process to reduce chemical consumption and wastewater production according to the MLD approach. Economic assessments have highlighted how the developed process can generate a high profit.

The full details are reported in **ANNEX 2**.

3. Recycling process optimization of printed circuit boards

Printed circuit boards (PCBs) are essential to any electronic waste. In automotive manufacturing industries, the use of PCBs inside a car is necessary for managing almost all the functionalities of a vehicle, and the trend has drastically increased in the last decades.

Various processes are used for PCB metallic content recoveries, using physical, pyrometallurgical, hydrometallurgical, and combined technologies. Pre-treatments and dismantling of the components play a significant role in the upgradation and efficient metal extraction from PCBs. Therefore, dismantling can be considered a necessary step before any other chemical treatment.

Deliverable 5.3, "Simulation and lab-scale testing of materials recovery processes", provided some information relating to the laboratory-scale treatments of numerous materials in the automotive sector using hydrometallurgical processes. The activities carried out in the ambit of Task 5.3 firstly involved a chemical characterization, also specific for each SMD of PCBs. Based on the obtained results, mainly in terms of gold and copper content but also regarding the different shapes of each component, different recycling routes are defined. Then, some components that need to be removed from the boards have been identified as they inhibit dissolution yields. Other components with high content of gold, superficially exposed, can be treated by a hydrometallurgical process to recover the metal values. The rest of the board can be subjected to another hydrometallurgical process after preliminary physical treatment of particle size reduction.

Related to the activities on Task 5.4, Annex 3 presents a detailed analysis of the characterization of PCBs and their components, especially in dashboards, and provides process optimization for selective recovery of precious and base metal contents using two patented processes of GOLD-REC 1 (GDR1) and GOLD-REC 2 (GDR2). Process optimization was studied by factorial experimentations and adopting an MLD approach to reduce wastewater production. Finally, mass and energy balance are described, each output was characterized, and the economic sustainability was evaluated.

The full details are reported in **ANNEX 3**.

4. Recycling process optimization of Indium-Tin Oxide glass from Liquid Crystal Displays

The optimization of the hydrometallurgical process for the ITO glass recycling was performed with two kinds of samples containing 0.071 kg/t and 1.186 kg/t of Indium.

Detailed characterization of the input and all the process outputs has been performed using different analytical techniques such as ICP-OES, XRD, and XRF.

The waste processing process was divided into two main steps: extraction of Indium from glass and its subsequent extraction from leaching solution as a finished product.

The first part of the study consisted of three sets of experiments: pre-treatment (neutral leaching) and acid leaching (direct leaching, cross-current leaching with acid recycling, and counter-current leaching process). The main goal was to find optimal conditions and modes for the leaching process (solid-liquid ratio, the concentration of sulfuric acid, and organizing of the leaching process) to have maximum indium recovery from ITO glass at minimum reagent consumption.

The second part of the study was to find the best method for indium recovery from the leaching solution. The following methods were studied: precipitation with NaOH, electrowinning, and ion exchange.

Based on the hydrometallurgical process optimization results, process analysis was made to propose an Indium recycling process to reduce chemical consumption and wastewater production. Economic assessments have highlighted how the developed technique can generate a high profit.

Annex 4 presents a detailed analysis of the characterization of the studied ITO glass and provides process optimization for indium recovery. Finally, mass and energy balance are described, each output was characterized, and the economic sustainability was evaluated.

The full details are reported in **ANNEX 4**.

Abbreviations

FTIR	Fourier Transform Infrared
GDR1	Gold-REC 1 patent
GDR2	Gold-REC 2 patent
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IMSE	In-Mold Structural Electronics
ITO	Indium Tin Oxide
KETs	Key Enable Technologies
MLD	Minimum Liquid Discharge
P&ID	Process and Instrument Diagram
PCBs	Printed Circuit Boards
SMDs	Surface-Mount Devices
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

TREASURE

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Annex 1 – Pilot-scale reconfiguration

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1. Introduction

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The pre-existent mobile pilot plant was realized in a 40 feet container. It was intended for the treatment of ground electronic board powders with a maximum size of 2 mm.

A detailed study was done to identify the pilot plant's possible implementations, starting from some critical issues shown during the experimental activities carried out as part of the FENIX project. One of the scopes of the reconfiguration was to modify and implement the plant in order that can process the materials of interest in the TREASURE project. More generally, the aim was also to make the plant more flexible for the treatment of different types of materials, not only powders. Therefore, more chemical reactors and filtration systems with different characteristics compared to those already present were added. Finally, all the valves were automated according to Industry 4.0.

The company engaged in carrying out the pilot plant reconfiguration was B.F.C. Sistemi S.r.l., the same company that built the plant in June 2019, so it was selected for economic and logical reasons.

Moreover, after the pilot plant's reconfiguration, start-up tests with water and a powder of printed circuit boards were done to check the correct working of all the equipment.

2. Pre-existent hydrometallurgical pilot plant

The pre-existent hydrometallurgical pilot plant was in an industrial site (Lorusso Estrazione S.r.l.) in Avezzano, about 50 km far from the University of L’Aquila. The pilot plant has been realized inside a mobile container that could be moved to several SMEs to test and demonstrate the technical feasibility of the hydrometallurgical processes.

The P&ID of the pilot plant is shown in Figure 1.

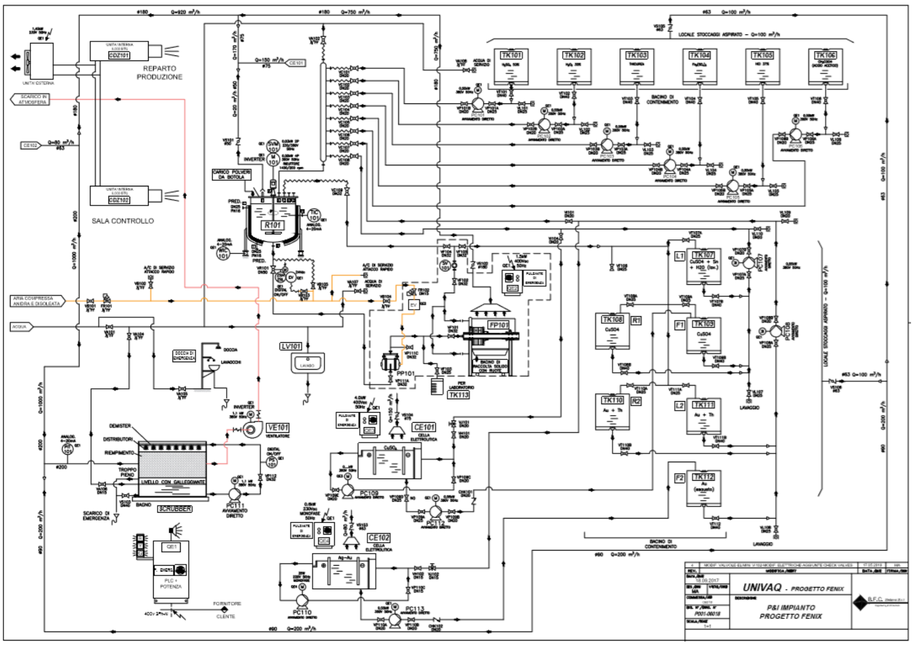

Figure 1: P&ID of the FENIX pre-existent hydrometallurgical pilot plant

The 40 ft container is composed of three different areas:

a. Storage area
b. Operating process area
c. Control panel area

Figure 2 report the layout of the hydrometallurgical pilot plant.

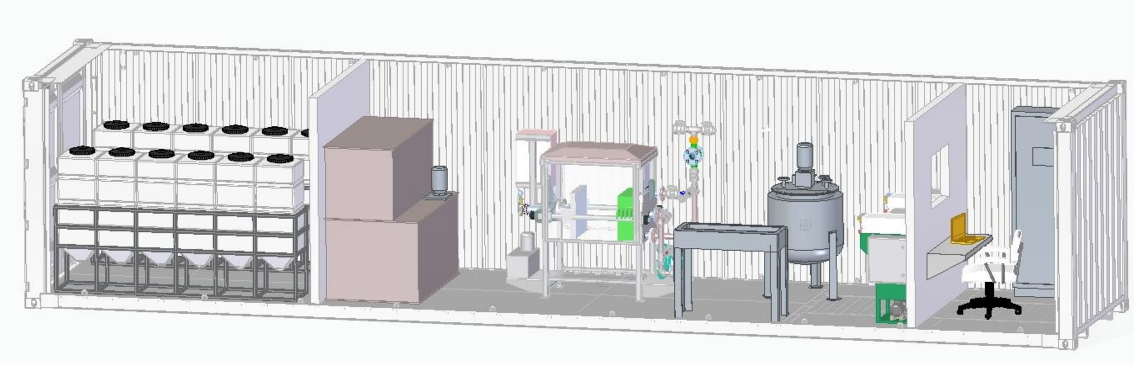

Figure 2: Layout 3D image of the FENIX hydrometallurgical pilot plant

Figure 3 shows a picture of the pilot plant in the industrial shed of Lorusso Estrazione S.r.l. company to the left side, while to the right side the elevation and the plan views are showed.

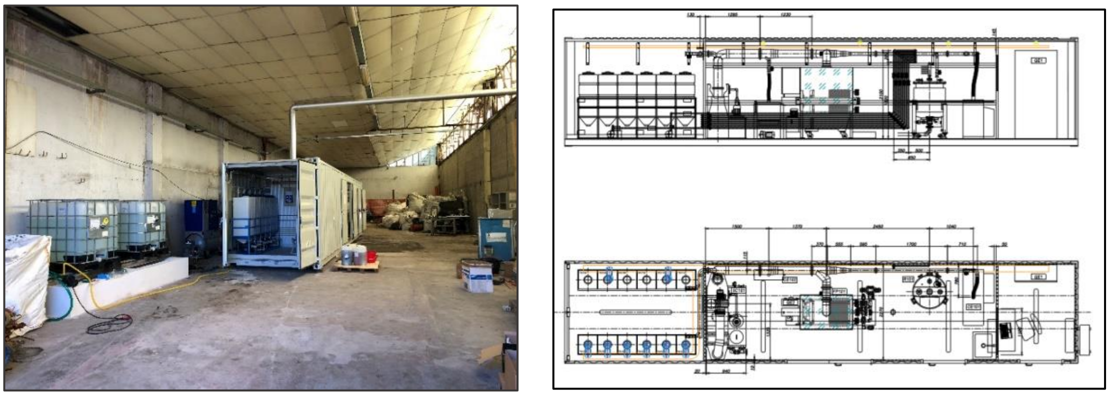

Figure 3: Picture of the hydrometallurgical pilot plant to the left side and the elevation and plan views to the right side

2.1 Storage area

The storage area consists of 12 tanks with a capacity of 200 litres with a total of 8 centrifugal pumps for solution transfer. In this area occurs both the storage of chemicals and the temporary storage of the processing solutions. The tank of each chemical had a specific pump, while for the tanks of the processing solutions, there was a pump in service of three tanks since the leaching solutions were mainly of two types. Chemicals were fed into the tanks via a mobile pump, but without fixed piping, as the 1 m^3 caged IBC of the chemicals were placed outside the container. In Figure 4 is shown the storage area, the tanks for the processing solutions are located on the left side, while the tanks for the chemicals are on the right side.

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Figure 4: Storage area of processing solutions and chemicals

Chemical tanks are named TK101-TK106. To transfer chemicals in reactor or in other external tanks, each tank is equipped with a centrifugal pump (PC101-PC106), launched via software, making sure that all the valves along the pipes are open. Manual valves (VP101A-VP106A) and (VP101B-VP106B) are installed on suction and delivery pipe, this last allows to adjust the flow rate. In addition, each tank installs a manual valve (VT101-VT106), and another manual valve (VL101-VL106) allows the chemicals to transfer to other tanks outside the plant.

Processing solutions storage tanks are named TK107- TK112. Processing solutions can be transferred with the use of two different centrifugal pumps controlled via software. Pump PC107 is connected to TK107, TK108, and TK109, which only transfers copper solutions. Instead, pump PC108 is connected to TK110, TK11, and TK112 to manage the gold solution. The flow rate in delivery pipes is regulated by VP107B and VP108B, while in the suction pipes, there are two manual valves, VP107A and VP108A. At the bottom of each tank, a manual valve transfers the flow in the pipes (VT107B-VT112B), while VL107 and VL108 allow the solution to transfer to other external tanks.

2.2 Operating process area

In this area, the chemical operations necessary for the execution of hydrometallurgical processes take place. A list and a brief description of the main equipment are below reported:

a. SCRUBBER: equipment for gaseous emissions abatement. All the equipment in the operating process area, such as all the storage area, are under suction. It is necessary to add soda solution for neutralization and verify the liquid level before each launch of the plant. It is constituted by a filling bath of 556 litres equipped with a float with an emergency drain. In case of overflow, discharge the solution in an emergency drain. Fan and recirculation pumps are launched via software. Failure to start this equipment blocks any other operation.

b. CHEMICAL REACTOR (R101): is the only chemical reactor of the plant. It is used to carry out solid-liquid extraction. Its useful volume is 200 litres, it is internally coated in ebonite for acid resistance. Equipped with an agitator (M101) that allows the mixing of solutions (maximum speed 250 rpm). Solid feed is manual, while water and chemicals are loaded by opening manual valves and automatic pumps. Reactor discharge is controlled by a solenoid valve (VR101) managed via software. In addition, a weight cell allows to show the weight in the reactor through a display.

c. PLATE&FRAME FILTER (FP101): equipment used for liquid and solid separation from suspension obtained by leaching treatments. Once the correct number of plates is selected based on the solid of the suspension, you can manage the filter press by electrical cabinet QE1, the pump (PC112) will be automatically started, and the filter press closing cycle will be completed.

d. COPPER ELECTROLYTIC CELL (CE101): it is used for the copper electrowinning process. The cell is constituted by a bath of 178 litres and equipped with 10 copper cathodes and 10 titanium coated by mixed oxides anodes alternately arranged. Three-phase rectifier display (QE3) can regulate current up to a maximum of 350 A, while the voltage can be measured during the operation. Solution rich in copper can be loaded by TK107, TK108, and TK109. Recirculation of the solution occurs through pump PC109, controlled by the rectifier. The discharge occurs with pump PC112 (controlled by software) opening the valves along the pipe that return to TK109.

e. PRECIOUS METALS ELECTROLYTIC CELL (CE102): it is used for the gold and silver electrowinning process. The cell is constituted by a bath of 20 litres and equipped with one copper cathode and two titanium coated by mixed oxides anodes. Three-phase rectifier display (QE3) can regulate current, while the voltage can be measured during the operation. Solutions rich in gold and silver can be loaded by TK110, TK111, and TK112. Recirculation of the solution occurs through pump PC110, controlled by the rectifier. The discharge occurs with pump PC113 (controlled by software) opening the valves along the pipe that return to TK112.

Figure 5 shows some pictures of the main equipment of the operating process area.

(a) (b)

(c)

Figure 5: Pictures of the main equipment. a) chemical reactor; b) copper electrolysis cell; c) plate & frame filter

2.3 Control panel area

The plant is controlled by PLC (Programmable Logic Controller), but you can work in semi-automatic mode, in fact only the pumps are launched via software, but almost all the valves must be manually opened/closed, except of the VR101 valve that manage the discharge of the chemical reactor. In the control panel area, there are:

a. ELECTRICAL CABINET: the plant's main switch is equipped with manual selector switches that allow managing different equipment in manual or automatic mode.

b. COMPUTER WORKSTATION: software that manages the control of scrubber, automatic valves, and pumps. You can also insert different procedures of hydrometallurgical treatment by adding quantities of chemicals, water, and solids. If the total volume exceeds the useful volume of the reactor, the software prevents you from starting the treatment. During a test, a series of messages appear on the screen indicating which valves to open or close during each operation.

In Figure 6, the electrical cabinet and the computer workstation are shown.

Figure 6: Pictures of the control panel area.

3. Main objectives of the reconfiguration

The reconfiguration of the hydrometallurgical pilot plant aims at solving the main issues that emerged during the experience of the FENIX project in the use of the pilot plant, at making the plant more flexible for the treatment of different types of materials, and more specifically at adapting to the materials of interest for the TREASURE project.

The experimental pilot-scale activities carried out during the FENIX project were mainly related to the treatment of printed circuit boards' powders with a particle size below 2 mm. These tests showed the following critical points to be solved during the reconfiguration:

a. Clogging of the suction pipes during the chemical reactor discharge upstream of the plate & frame filter.
b. The plant's only filtration system, the plate & frame filter, was unsuitable for retaining small quantities of solid and, specifically, particles with small particle sizes, such as gold particles and generally all the metals recovered by precipitation.
c. From the point of view of operations carried out by the operators, the use of an external mobile pump to transfer chemicals from the caged IBC to the corresponding tank (TK101-TK106) was not a good safety practice.

In Figure 7 the clogging of the suction pipes and of the pneumatic diaphragm pump located in the line were shown.

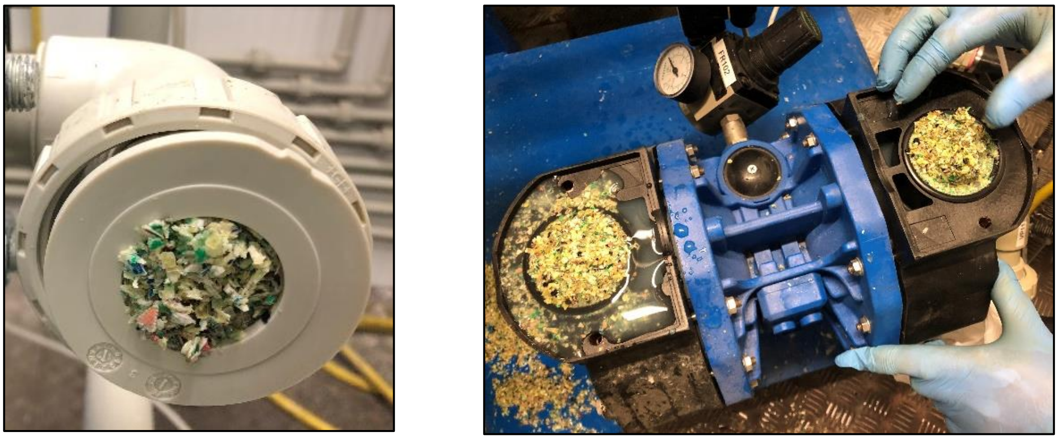

Figure 7: Clogging of the pipeline and pump during the discharge of the chemical reactor.

It depended on the long horizontal path of the suction pipes and on the chemical reactor position not high enough, so that the suspension remained clogged even inside the reactor on the bottom at the discharge. An attempt to resolve has been carried out by adding a small tube that guaranteed a discontinuous air insufflation to slightly raise the suspension during the discharge and avoid clogging. This has not helped to completely solve the issue. Therefore, the problem of clogging remained in the case of high amounts of solid in the suspension to be discharged from the reactors and for materials with a high specific density as the printed circuit board powders. To avoid clogging, the following actions could be considered:

a. The chemical reactor is placed on a chassis in such a way that it is raised from the ground, and there is also a higher force of gravity that makes the transfer in the pipes easier.
b. The suspension was directly discharged in a vacuum filter like the bag filters.
c. Design of a chemical reactor with different characteristics that allowed to avoid removing the solid from the reactor at each process operation.

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Moreover, as mentioned earlier, the reconfiguration was focused on making the pilot plant more flexible to process other materials without physical size reduction pre-treatment and the materials of interest for the TREASURE project. The materials studied at the lab scale in the ambit of the present project are:

a. In-mold structural electronics (IMSEs)
b. ITO glass
c. Printed circuit boards (PCBs) from the combi-instrument

In Figure 8 are shown the IMSEs and ITO glass samples.

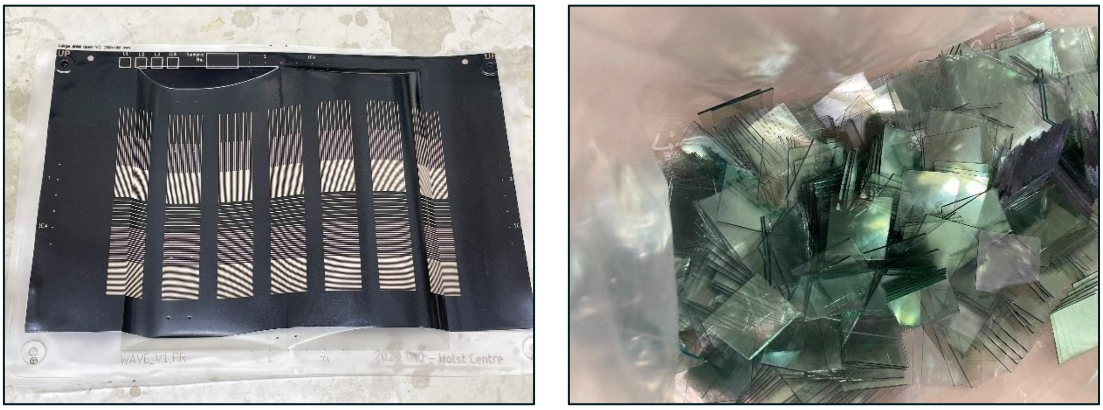

Figure 8: Photographic aspect of IMSE and ITO glass samples.

Based on the status of the element of interest to be recycled from these samples for their hydrometallurgical treatment, no preliminary grinding stage is required. IMSEs are composed of a silver ink layer directly on the surface of the samples so that it is already exposed to the action of acids to be dissolved. ITO glass samples are composed of a glass substrate coated by an ITO layer on both sides; compared to the initial sample, the material was supplied by EuroLCDs after being cut into squares of about 2 cm. From a chemical point of view, no grinding would be necessary to ensure the dissolution of indium and tin during the leaching phase, but only a reduction in sample size for easier solid handling during the hydrometallurgical process.
Regarding the PCBs, the two developed hydrometallurgical processes require a disassembly step to separate some SMDs from the board. Some residual components, such as ICC, remain on the board, which is subjected to a grinding step until a particle size of less than 2 mm is achieved. Therefore, two materials of different characteristics have to be treated from the PCBs. Figure 9 shows a mixture of SMDs and a sample of powders from PCBs.

Figure 9: Photographic aspect of powder on the left slide, and different SMDs on the right side from PCBs.

While the powders size particles are below to 2 mm, the SMDs from PCBs can have shapes and different size up to 5-10 cm. For these reasons, the treatment of SMDs can be assimilated, from the point of view of suitable technologies, to the previous materials as IMSE and ITO glass. For the treatment of the powders, instead, it is necessary to take into account the considerations to solve the issue of clogging during the discharge of the chemical reactor.

4. Reconfigured TREASURE hydrometallurgical pilot plant

In the present section the main implementations and the description of all the added equipment in the reconfigured hydrometallurgical pilot plant are reported. For each equipment its functionalities are explained, and technical data are provided as well as pictures taken within the reconfigured plant. Process and Instrument diagram (P&ID) displaying the equipment, the piping components (valves, pumps) and the controllers, was produced for the TREASURE reconfigured pilot plant (**ANNEX 1.A**).

The Declaration CE of Conformity for the reconfigured plant (serial number 19003, year of construction 2019, and subsequent revamping carried out in 2022) has been issued, complying with provisions of European Directive 2006/42/EC.

4.1 Main implementations

To achieve the objectives explained in section 3, the main implementations carried out have been listed below:

a. Addition of two chemical reactors with different characteristics.
b. Addition of different filtration systems, such as cartridge and bag filters.
c. Movement of the chemical storage tanks to an external area directly connected to the plant by a pipeline.
d. Automatization of all the valves according to Industry 4.0
e. PLC software revising with specific recipes for the materials of interest for the TREASURE project.

The first two implementations are realized to the left side of the container plant by removing the chemical tanks. In Figure 10, on the left side, a picture taken during the works shows the freed space for adding chemical reactors and filtration systems in the storage area of the pre-existent pilot plant. On the right side, a picture of the pilot plant after the reconfiguration from which you can observe the chemical caged IBCs directly connected to the main equipment with piping.

Figure 10: Picture of the plant during and after the reconfiguration works.

4.2 New added equipment

In this section a list of the added equipment to the existing pilot is reported, for each equipment dedicated details engineering documents are provided. Moreover, overall plant layout and process and instrumentation diagram (P&ID) are also shown.

The layout of the reconfigured hydrometallurgical TREASURE pilot plant is shown in Figure 11.

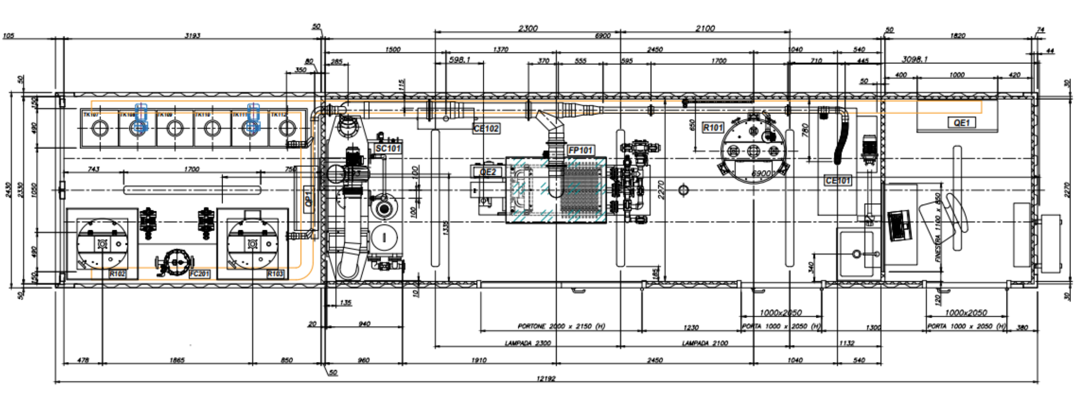

Figure 11: Layout of the reconfigured hydrometallurgical pilot plant, plan view.

You can see on the left side the area where the major changes were made, with the addition of two chemical reactors and different filtration systems. However, the reconfiguration involved the whole plant for the connections of the pipes and the automation of all the valves. In addition, a filtration system has also been added for the pre-existing chemical reactor, located in the middle area, so that depending on the type of filtration desired, the plate & frame filtration or the cartridge filter can be used.

Below is the list of the main and auxiliary equipment added to the pilot plant:

a. Chemical Reactor (R102)
b. Chemical Reactor (R103)
c. Pneumatic diaphragm pumps (PP201, PP301)
d. Bag filter (FC201)
e. Cartridge filters (FC101, FC202, FC301)
f. Automatic valves
g. Level indicator transmitters (LIT101-LIT112)
h. Level switch high (LSH101, LSH102)

4.2.1 Chemical Reactor R102

The chemical reactor R102 is like a slurry reactor intended for the treatment of ground materials with small particle sizes, its useful volume is 100 litres. The stirrer reaches almost the bottom of the reactor so that good mixing of the suspension can be guaranteed. To avoid the issues related to the powders clogging during discharge, filtration is ensured by a big filter, and the chemical reactor position is higher than the ground floor.

This type of reactor can also be used for the chemical operations like cementation and precipitation to recover metals from the leach liquor solutions or for the preparation of leaching solutions before starting contact with the material to be treated.

In Figure 12, a picture of the chemical reactor as well as an extract of the P&ID, are shown.

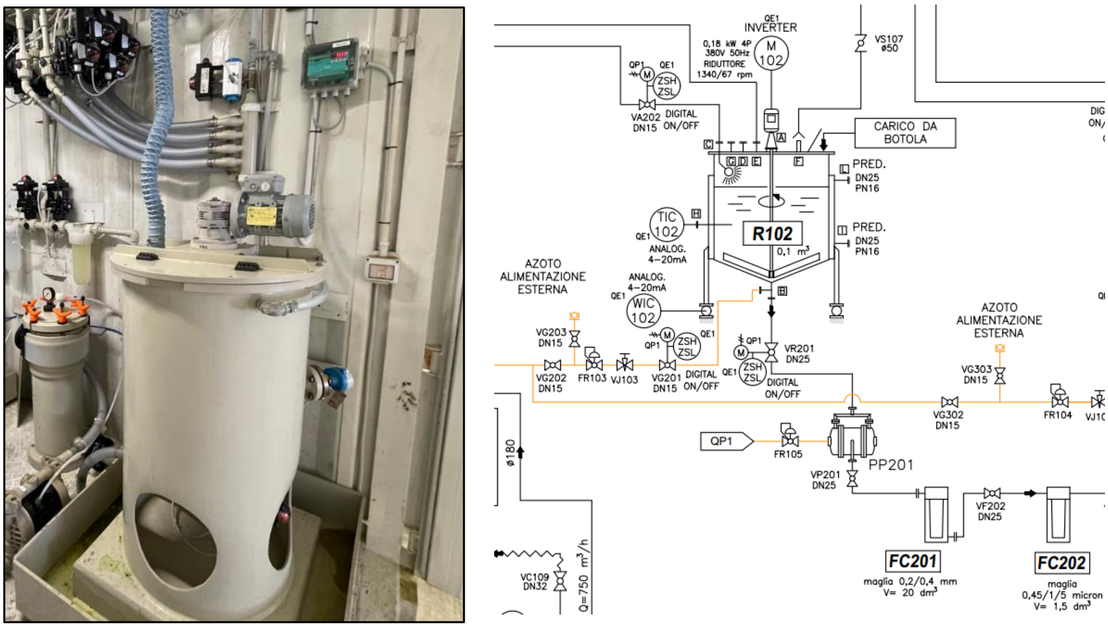

Figure 12: Picture of chemical reactor R102 and an extract of P&ID.

From the P&ID extract it is possible to observe the presence of an insufflation line of gases that can be air or nitrogen depending on the reagents that are used. Then for the discharge operations a pneumatic diaphragm pump (PP201) allows the suspension to be transferred to the filtration systems. Based on the specific objectives, like the amount of expected solid to be recovered and particle size, can be used bag and cartridge filters with different openings and materials. As you can see from the P&ID, the following filtration systems are in line, you can work with both or decide to exclude one of the two. Regarding the controllers, the reactor is equipped with an instant temperature indicator (TIC102) and a weight indicator (WIC102). In addition, is prepared for the cooling coil installation. Then, there is also a device that sprays water in order to ensure proper washing of all the reactor's internal surfaces.

In Table 1, the design data are reported.

Table 1: chemical reactor R102 design data

R102 – chemical reactor design data	
Vessel construction material	Polypropylene
Cooling coil material	Prepared for the installation
Propeller construction material	Polypropylene
Useful volume	100 litres
Design pressure	ATM
Operating pressure	ATM
Design temperature	0 - 60 °C
Maximum operating temperature	50 °C
Weight cell	Yes
Solid loading	Manual
Solution loading	Centrifugal pumps
Discharge of the suspension	Pneumatic diaphragm pump
Insulation	No
Inspection	Yes

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The stirrer is with servo-ventilated electric motor for inverter and gearbox use, and the propeller is a rotor with 2 fixed "V" blades straight. In Figure 13, the technical drawing design of the chemical reactor is shown.

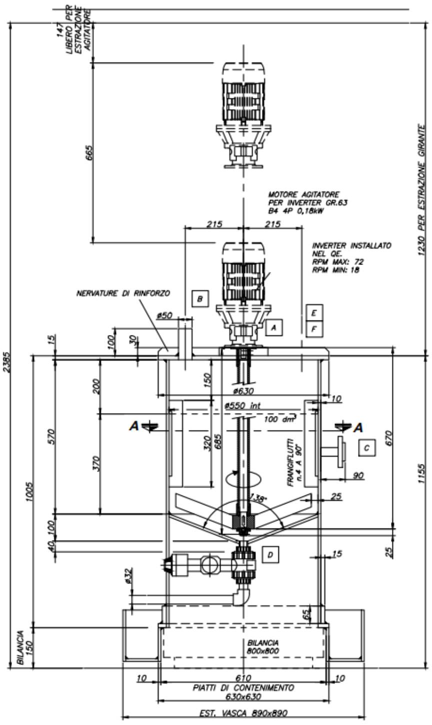

Figure 13: Technical drawing design of chemical reactor R102.

Then, the Declaration CE of Conformity for the chemical reactor R102 (serial number 22004, year of construction 2022) has been issued.

4.2.2 Chemical Reactor R103

The chemical reactor R103 is intended for the treatment of materials without any grinding or heavy powders that can create problems during the filtration, its useful volume is 100 litres. It is a reactor specially designed to prevent that the solid is removed from the reactor for each filtration operation. Inside the reactor, towards the bottom, is located a septum with several openings of 1.2 mm that allow the passage of the solution but not of the solid, so the solid remains inside until the end of the process. During the filtration, the septum retains most of the solid so that issues related to clogging pipes are avoided. The stirring, if necessary, takes place through air/nitrogen insufflation. Nevertheless, there is a stirrer with a servo-ventilated electric motor use and gearbox, but its function is exclusively related to material discharge at the end of all leaching operations; it is not used to mix the suspension during chemical reactions occur. A rotor with 2 curved fixed blades allows the solid conveying in automatic mode for the discharge through an inspectable side door.

In Figure 14, a picture of the chemical reactor as well as an extract of the P&ID, are shown.

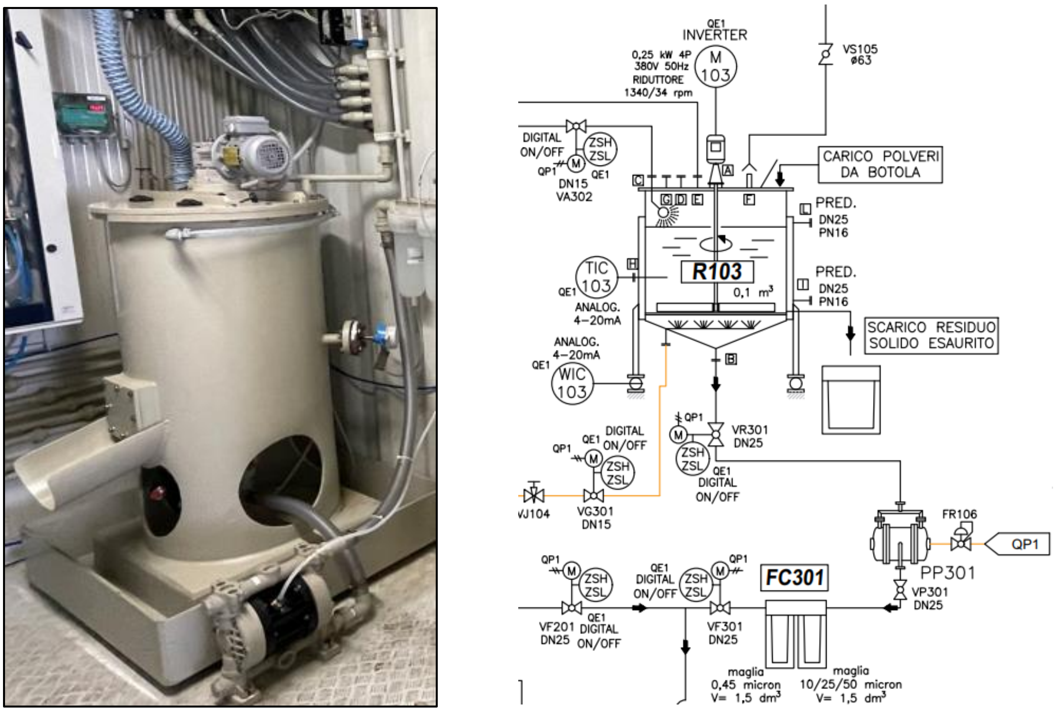

Figure 14: Picture of chemical reactor R103 and an extract of P&ID.

From the picture you can see the hatch for discharge of the solid from the reactor and the slide to collect the material. Then, from the P&ID extract it is possible to observe the presence of an insufflation line of gases that can be air or nitrogen depending on the reagents that are used. For the discharge operations a pneumatic diaphragm pump (PP301) allows the suspension to be transferred to the filtration systems. In this case, since the presence of the septum only low amount and small particles are sent to the filters. Two cartridge filters are connected to the pipes. Filters with different openings and materials can be used based on the solid to be recovered. Regarding the controllers, the reactor is equipped with an instant temperature indicator (TIC103) and a weight indicator (WIC103). In addition, a Teflon cooling coil can manage the temperature during the reactions. In Figure 15 is shown a picture of the inside of the chemical reactor in order to highlight the septum and the cooling coil.

Figure 15: Internal view of the chemical reactor R103.

The reactor is also equipped with a device that sprays water in order to ensure proper washing of all the reactor's internal surfaces. In Table 2, the design data are reported.

Table 2: Chemical reactor R103 design data

R103 – chemical reactor design data	
Vessel construction material	Polypropylene
Cooling coil material	Teflon
Propeller construction material	Polypropylene
Useful volume	100 litres
Design pressure	ATM
Operating pressure	ATM
Design temperature	0 - 60 °C
Maximum operating temperature	50 °C
Weight cell	Yes
Solid loading	Manual
Solution loading	Centrifugal pumps
Discharge of the suspension	Pneumatic diaphragm pump
Insulation	No
Inspection	Yes

Technical drawing design of the chemical reactor is shown in Figure 16.

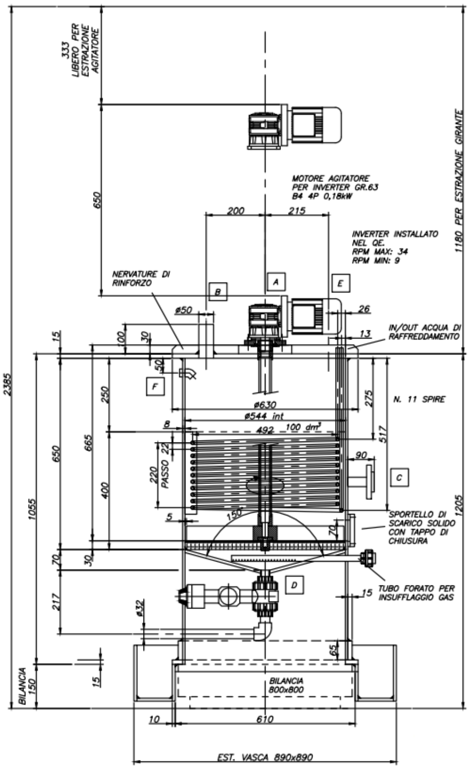

Figure 16: Technical drawing design of chemical reactor R103.

Then, the Declaration CE of Conformity for the chemical reactor R103 (serial number 22005, year of construction 2022) has been issued.

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4.2.3 Pneumatic diaphragm pumps

Pneumatic diaphragm pumps (PP201 and PP301) have been added to service of the two new chemical reactors. They are pneumatic volumetric double diaphragm pumps, designed and built for pumping liquids chemically compatible with the construction materials of the pump, polypropylene. They are self-priming; when starting, the pipes can be empty. The pump supplier company was Deltagalvano and the model is Boxer 81 PP. In Figure 17 a picture of the pump and its technical drawing design are shown.

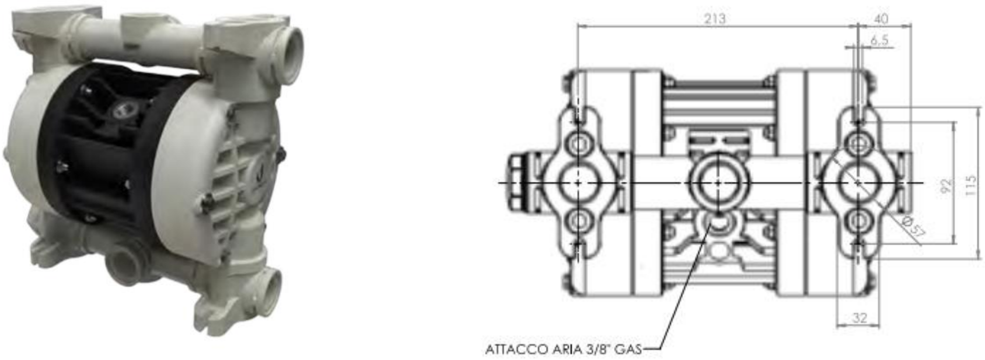

Figure 17: Picture and technical drawing design of pneumatic diaphragm pumps.

The pumps are directly launched by PLC software. In Figure 18, pump performance curves show head vs flow rate as a function of different air supply pressure. Also, the curves related to the air consumption are reported.

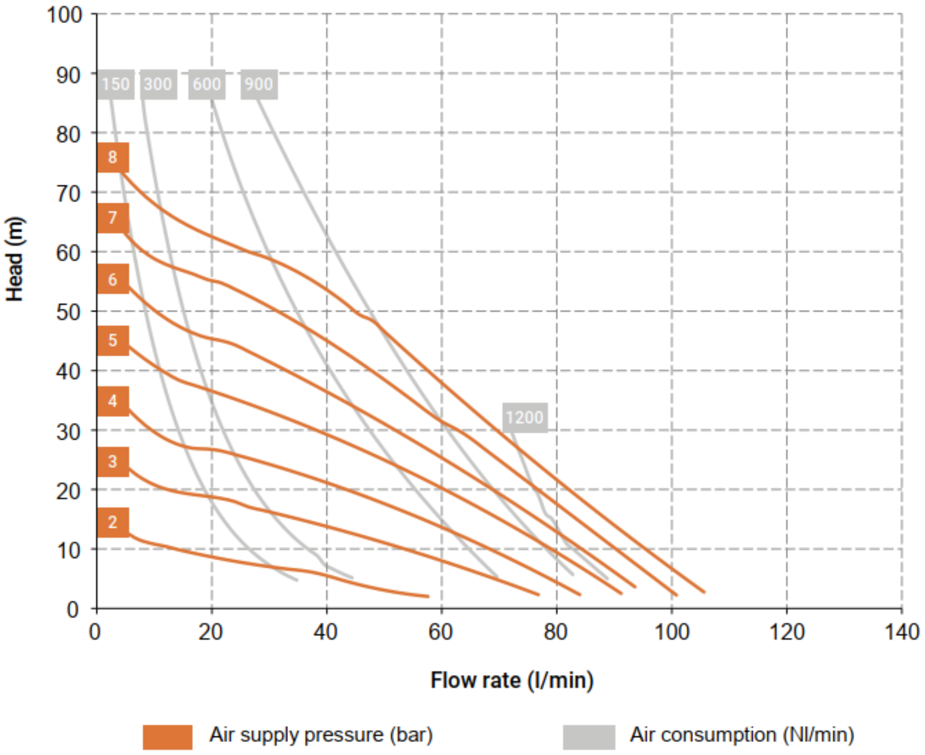

Figure 18: Pump performance curves.

4.2.4 Bag filter

The bag filter FC201 is in service of the chemical reactor R102. It is inserted in a basket to support the filter medium, and a compression ring makes the seal. The fluid flows through the bag filter from the inside, and the solids are retained inside. The capacity is 20 liters, both the filter and the basket are made of polypropylene. Based on the specific application different opening filters are available (ten with opening size of 200 µm and two with 5 µm). In Figure 19, a picture and technical drawing design are shown.

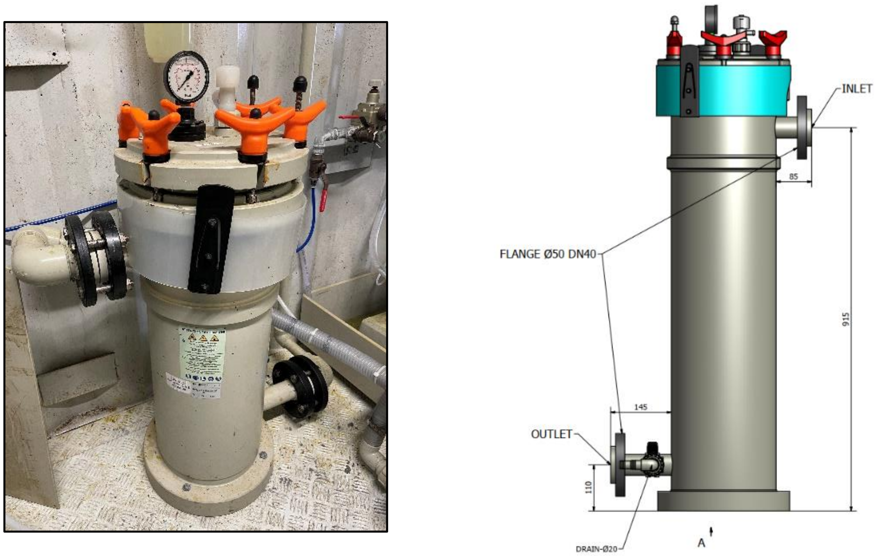

Figure 19: Picture and technical drawing design of bag filter.

The construction company was the Envirogen Group. The filtering surface is 0.49 m^2. In Table 3 the chemical resistance characteristics of the bag filter are reported.

Table 3: Polypropylene bag filter resistance.

Bag filter materials: polypropylene	
Maximum operating temperature	90 °C
Use for aromatic solvents	No
Use for aliphatic solvents	Yes
Use for aqueous solutions	Yes
Use for acid solutions	Yes
Use for strong acid solutions	Yes
Use for alkali solutions	Yes
Use for strong alkali solutions	Yes
Use for vegetable/animal oils	Yes

4.2.5 Cartridge filters

Four cartridge filters are added in the plant. The filter FC101 was added to process the suspension from the pre-existing chemical reactor R101 to provide an alternative to the plate & frame filter. The filter FC202 was installed in the discharge pipeline of chemical reactor R102, downstream of the bag filter, to also retain small particles, for example, from metals precipitation treatment. Then, FC301 is composed of two cartridge filters in such a way that particles of different sizes can be retained and separated from each other by selecting filters with specific mesh openings.

Filtration in cartridge filters consists of the forced passage of the solution through a porous medium. All the installed cartridge filters have a capacity of 1.5 liters. Filters are available in ceramic or polypropylene, with replaceable filters with openings of 5, 10, and 25 µm for polypropylene filters and 0.45 µm for ceramic filters. In Figure 20, a picture of the installed cartridge filtration system (FC301) and the filtering medium are shown.

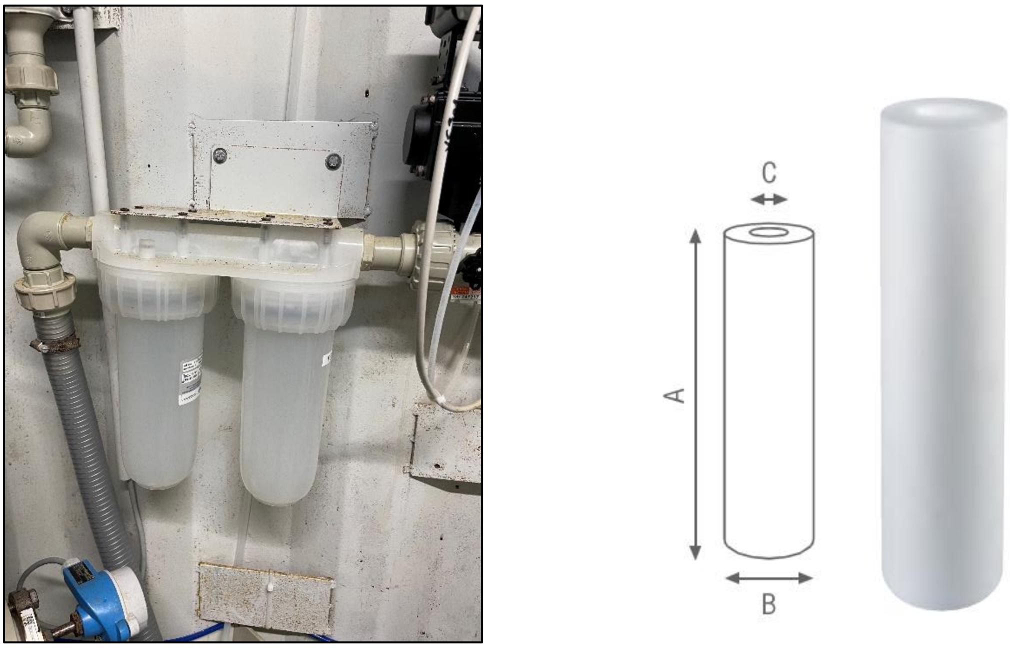

Figure 20: Cartridge filters FC301 on the left side and the filtering medium on the right side.

In Table 4 the flow rate and geometric characteristics of the available filters are reported. Maximum operating temperature is 80 °C.

Table 4: Cartridge filters characteristics

				size, mm		
code	**model**	**height**	**flow rate, L/h**	**A**	**B**	**C**
RA5706508	CPP 10 SX – 5 mcr	10”	2000	250	61	28
RA5706509	CPP 10 SX – 10 mcr	10”	2000	250	61	28
RA5706511	CPP 10 SX – 25 mcr	10”	2000	250	61	28
RA5265102	AB10SX – 0.45 mcr	10”	300	250	70	30

4.2.6 Automatic valves

The pre-existing manual valves have been replaced with automatic valves to conduct the operations necessary for the process execution automatically directly from the computer workstation via PLC software, according to Industry 4.0.

Regarding the working of the automated valves, a mechanical device uses a power source to operate a valve. In the present case, the power source is pneumatic, by compressed air. The two-way ball’s actuator produces the rotational motion needed to operate rotary valves. So, it operates by converting the linear motion of a cylinder piston into the stem drive's rotational motion. The boxes SB series of Aliaxis are installed in the plant, they are primarily instruments to indicate the position with direct viewing through an open/closed indicator and/or through the remote signal output from the switch inside the box. Figure 21 shows how their work and a picture of their installation in the pilot plant.

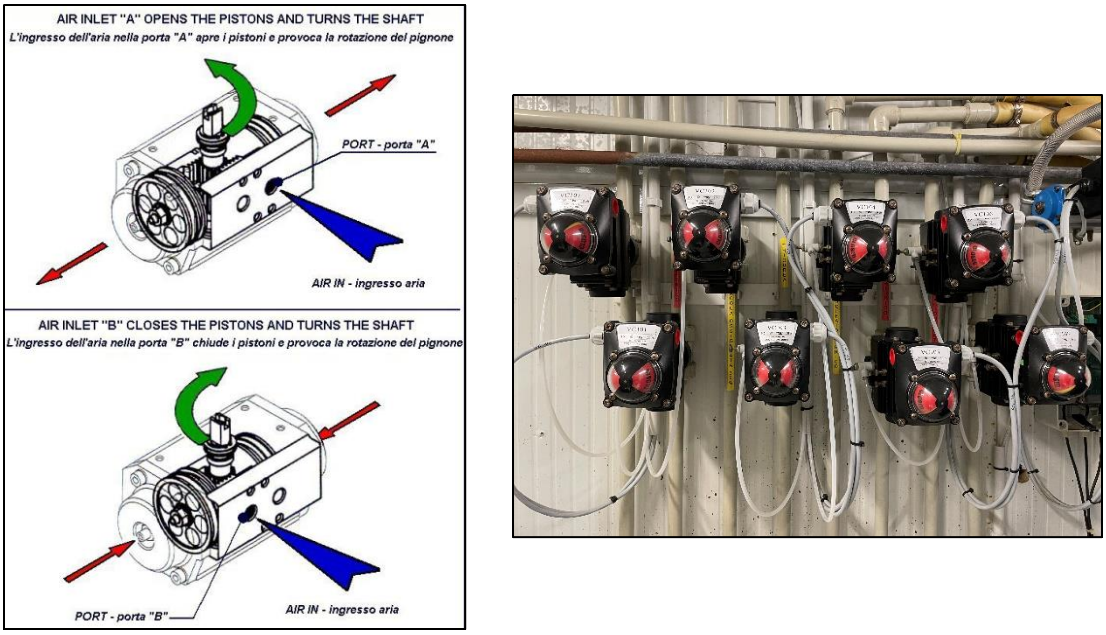

Figure 21: Pneumatically actuated 2-way ball valve working and their installation in the plant.

In addition, for some of the installed automatic valves it is possible to partial the flow to adjust the flow rate in an opening between 10 and 90 degrees.

4.2.7 Controllers

Level indicator transmitters (LIT101-LIT112) are sensors with an electrical transmission output for remote indication of liquid. They were installed on the chemical caged IBC (TK101-TK106) and on the operating solution provisory storage tanks (TK107-TK112). The working of the LIT is by radar, it measures the distance from the transmitter, located on the top of the tanks, to the surface of the liquid located farther below in much the same way as ultrasonic transmitters by measuring the time of flight of a traveling wave. The signal output (4 – 20 mA) is displayed on the computer with the purpose of providing inputs to the PLC. More specifically, at the end of a chemical operation that is taking place in one of the reactors, you can directly select from the computer workstation the tank in which to discharge the filtered solution based on the volume to discharge and the free volume in the tank. In addition, if tanks with a lower free capacity than the volume to be discharged were chosen, the PLC would block the operation. In Figure 22, is shown a picture of the LIC installed on tank 107.

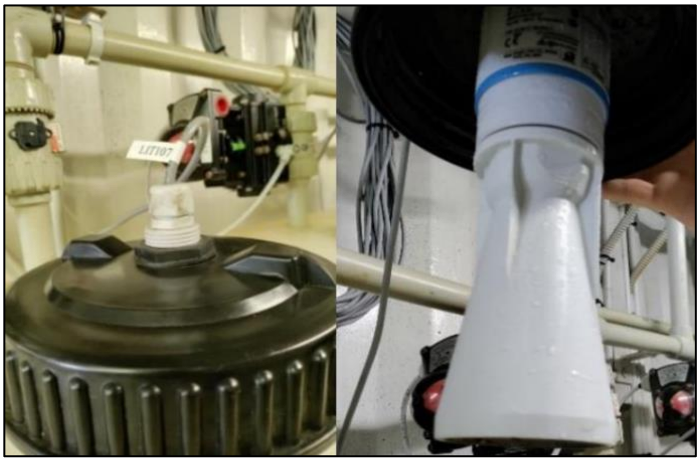

Figure 22: Picture of the level indicator transmitter installed on TK107.

Then, two level switch high (LSH101 and LSH102) are added to electrolysis cells (CE101 and CE102) to monitor the level in the baths. A LED lights up according to the different operating phases of the electrodeposition. Depending on whether the cell is empty, if loading is taking place or if you reach the maximum fill level different colours will light up: green, yellow and red. In Figure 23 is shown the LSH101 installed on the CE101 electrolysis cell.

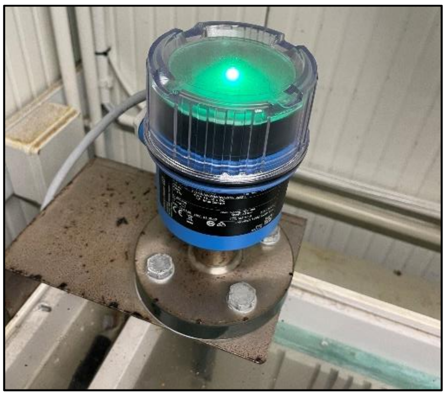

Figure 23: Picture of the level switch high LSH101 installed on CE101.

In addition to the substantial implementations just described, a complete maintenance of the plant was made to clean up the corroded surfaces. Moreover, the rectifiers of the electrolysis cells were sent to the supplier company to verify their correct functioning, and the filter press cake cart was replaced with a polypropylene one to prevent it from being corroded by chemicals, a picture is shown in Figure 24.

Figure 24: Picture of the plate & frame module in which you can see the polypropylene cart.

4.3 Pilot plant start-up test

Once the necessary modifications for the reconfiguration of the hydrometallurgical pilot plant have been completed, the plant has been again located in the industrial site of Lorusso Estrazione S.r.l. in Avezzano, about 50 km far from UNIVAQ.

In December 2022, start-up tests were carried out in order to check the correct working of all the equipment and to also investigate the new implementations of the PLC software. Therefore, blank tests with the use of the water but at the same time using waste similar by type to those of the TREASURE project were performed. The correct working of the chemical reactor R102 was tested with a powder of PCBs, with the aim of evaluating one of the main critical points that occurred in the pilot plant before the reconfiguration, which was the clogging during the discharge operation for powders with a high average density. Using the bag filter and the raised position of the reactor allowed the suspension to be discharged and separated from the solid in the correct way. Figure 25 shows images during the test on reactor R102 and of the software while another test on reactor R101 was being carried out.

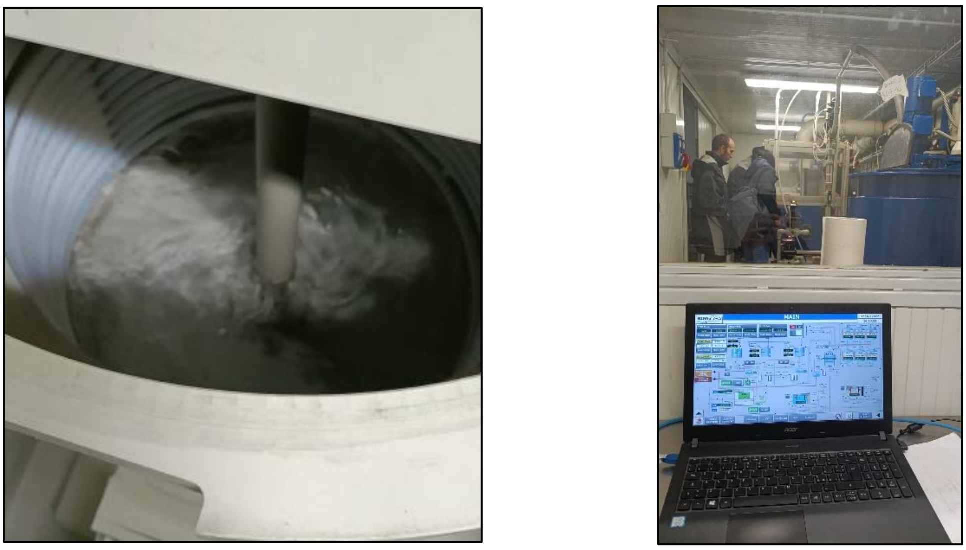

Figure 25: Pictures taken during the start-up test.

5. Conclusions

The reconfiguration of the pre-existent hydrometallurgical pilot plant had the following main objectives to be achieved:

a. Resolution of the main issues arising from the trials conducted under the previous European project.
b. Making the pilot plant more flexible for the treatment of different types of materials.
c. Adapting the plant to the TREASURE materials according to their type and the processes developed at lab-scale.
d. Fully automate the plant in such a way that it can be completely governed by PLC.

With the aim of achieving these objectives, the main reconfigure plant implementations concerned:

a. Addition of two chemical reactors with different characteristics.
b. Addition of different filtration systems, such as cartridge and bag filters.
c. Movement of the chemical storage tanks to an external area directly connected to the plant by a pipeline.
d. Automatization of all the valves according to Industry 4.0
e. PLC software revising with specific recipes for the materials of interest for the TREASURE project.

After the works had been completed, a start-up test was performed in order to check the correct working of all the equipment of the reconfigured pilot plant and to explore the operation of the PLC software on the basis of the chemical operations to be carried out to treat the TREASURE materials.

Abbreviations

CE	European Conformity
IBC	Intermediate Bulk Container
ICC	Integrated Circuit Chips
IMSE	In-mold Structural Electronics
LIT	Level Indicator Transmitter
LSH	Level Switch High
P&ID	Piping and Instrumentation Diagram
PCBs	Printed Circuit Boards
PLC	Programmable Logic Controller
SMDs	Surface Mount Devices
SME	Small Medium Enterprise

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.

REV.	MODIFICA /MODIFY	DATA /DATE	FIRMA /SIGN
3	VI102 CORRETTA A DN20 - CORRETTA POSIZIONE VI101	04.11.2022	MA
2	COMPLETAMENTO STRUMENTI E DATI ELETTRICI	04.03.2022	MA
1	MODIFICHE VARIE	08.02.2022	MA

DATA /DATE
10.11.2021

DIS /DWG
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VISTO /CHKD

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DIS. N° /DWG. N°
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SCALA /SCALE
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IMPIANTO PILOTA (ex FENIX)
PROGETTO TREASURE

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Engineering & Production

D5.4: Pilot-scale reconfiguration, testing and optimization of a materials recovery process

Annex 2 – Recycling process optimization of in-mold structural electronics

31/05/2023 (M24)

Authors: Nicolò Maria Ippolito, Francesco Vegliò, Marco Passadoro, Pietro Romano (UNIVAQ)

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TABLE OF CONTENTS

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1. Introduction

The present Annex describes the results related to the optimization of the hydrometallurgical process for the recycling of silver from IMSE samples whereby silver is directly exposed on the surface. In addition, a detailed characterization of the input and of all the outputs of the process has been performed using different analytical techniques such as ICP-OES, XRD, FTIR, and XRF. The characterization and the hydrometallurgical process were investigated on different types of IMSEs like thermoformed, full silver area, elongated, and a mixture of all the samples provided by TNO Holst Centre. In addition, the characterization was also performed on different SMDs located on the surface of some samples. Process analysis was made to propose a silver recycling process to reduce chemical consumption and wastewater production according to the MLD approach. Economic assessments have highlighted how the developed process can generate a high profit.

2. Materials and methods

The TNO-Holst Center and the advisory board member Genesink provided the materials for this activity. Based on the results obtained by D5.3 - Simulation and lab-scaled testing of the materials recovery processes, samples with silver on the surface not embedded in polymer layers were selected. Although these samples had this common characteristic, they were different in terms of polymer substrate, type of ink used, and silver content. In addition, other investigated samples were again with silver on the surface but also with small LEDs.

Firstly, the samples have been subjected to a semi-quantitative analysis performed by X-Ray Fluorescence (XRF) (Spectro Xepos); in this way a preliminary screening was obtained. Subsequently the samples have been also characterized, by a quantitative point of view, mainly to determine their silver content since hydrometallurgical processes are aimed at its recovery. To characterize the metal fraction samples were attacked by aqua regia, and the obtained solutions were analyzed by Agilent Technologies 5100 ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) to obtain the sample metal content. The quantitative ICP-OES analyses were also carried out on leaching solutions and solutions after the chemical attack of the solid residue of the process in such a way as to allow the calculation of extraction yields during the optimization phase of the hydrometallurgical process. In addition, ICP-OES was used to characterize the wastewater generated by the process and to determine the purity of the final product of the process after a chemical attack.

In addition, other analyses, such as X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR), were also carried out to assess the effect of the hydrometallurgical process on the substrate samples. XRD analysis was performed using Siemens D5000 Diffractometer, and the X-Ray diffraction patterns (copper anode) were acquired in the range 2-theta 10-70 degree.

For the electrodeposition tests, a supply current (Tektronix) was used; you can set up the voltage in the range of 0.1 - 36 V and measure the instantaneous current in the electrolytic bath. In this way, note the submerged surface of the electrodes it was possible to determine the current density. The electrodes used were cylindrical, copper cathode [1], and graphite anode. The distance between the electrodes was maintained at 2 cm.

Titration of thiourea in leaching solutions was performed by an iodometric method to reduce chemical consumption to optimize the hydrometallurgical recycling process.

3. Characterization

This section shows some images of the samples used for the optimization of the hydrometallurgical process aimed at silver recovery. In particular, information on their chemical characterization is provided.

3.1. IMSE samples

3.1.1 Sample 1 – thermoformed PC

IMSE thermoformed PC samples are composed of a polycarbonate substrate, different types of printed layers (black graphic ink and dielectrics) and silver ink that is bonded with a polymer additive. Silver is in the surface, directly accessible for the recycling operations. Figure 1 shows the photographic aspect of the sample.

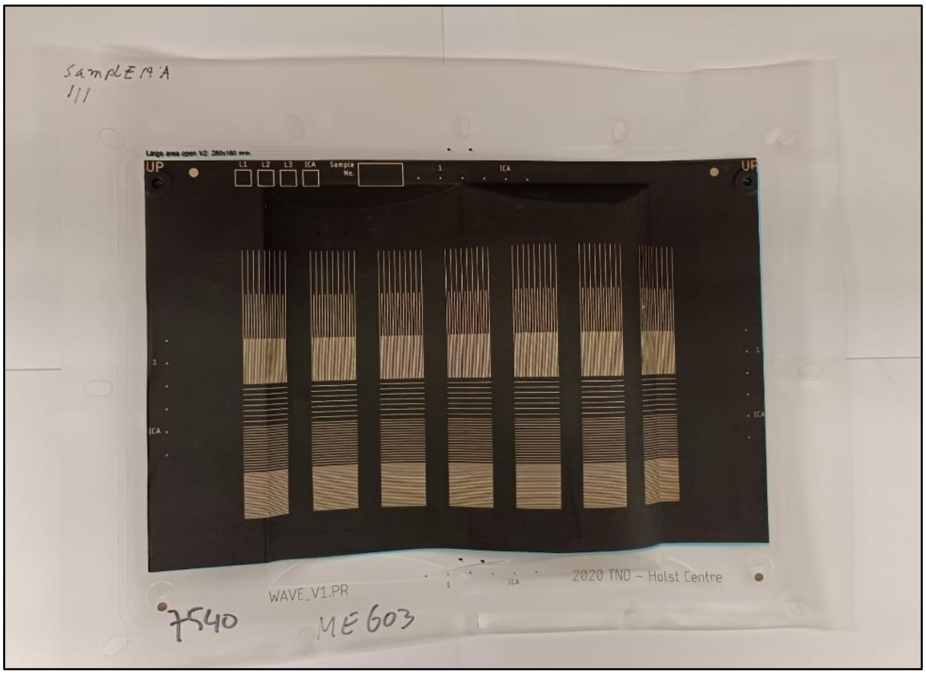


Figure 1: Photographic aspect of thermoformed PC - IMSE

The weight of each sample is in the range of 30 – 35 g for a sample size of 35x26 cm. Firstly, qualitative XRF analysis were carried out both in the black area and in the striped area where there is silver ink, according to the map in Figure 2.

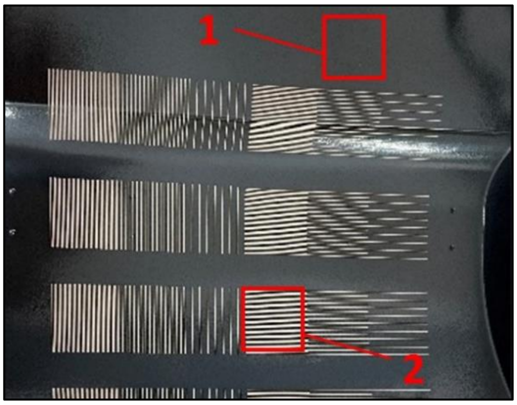


Figure 2: Map of performed XRF analyses

The analyses were carried out by cutting the pieces of the sample in according to the areas marked on the previous figure. It was possible to obtain a semi-quantitative analysis using the internal data libraries in the processing software. XRF analysis allowed to detect both metal fraction and the other fractions (plastics, organic compounds, etc.), the results are shown in Table 1.

Table 1: Semi-quantitative characterization of thermoformed-PC sample (XRF analysis)

Black graphic ink (area 1 in Figure 2)		Silver ink (area 2 in Figure 2)	
element	**concentration wt %**	**element**	**concentration wt %**
Fe	1.710	Fe	1.483
Mn	1.144	Mn	0.959
Si	0.522	S	0.612
S	0.386	Si	0.478
Ca	0.071	K	0.155
Ti	0.031	Ag	0.069
Cu	0.023	Cl	0.026
K	0.029	Cu	0.019
Cl	0.013	Ca	0.010

Based on the XRF results, the silver was determined exclusively in the striped area rows. In addition, among the elements most present iron and manganese are detected in both areas where the analysis was carried out. A concentration of less than 0.01 % was determined for elements not included in the table.

In addition, both qualitative and quantitative ICP-OES analyses were carried out. The metal fraction of the sample was dissolved by a double step chemical attack: firstly by nitric acid and then by aqua regia (HNO_3 : HCl 1:3 v/v). Qualitative and quantitative analyses have been performed on the solutions obtained by the chemical attack with the use of ICP-OES. A screening allowed to identify the most present elements and then the concentration was measured in the leach liquor in order to calculate the sample composition. Qualitative analyses showed that the main elements were present in the following order from most to least present: Ag, Fe, Mn, Ca, and Si; traces of Cu and Pb. ICP-OES quantitative results and their standard deviations are reported in Table 2.

Table 2: Quantitative characterization of thermoformed-PC sample (ICP-OES analysis)

Thermoformed-PC sample: quantitative analysis		
element	**concentration wt %**	**standard deviation wt %**
Ag	0.931	0.091
Fe	0.865	0.012
element	**concentration g/t**	**standard deviation g/t**
Pb	462	78
Ca	207	27
Mn	193	32
Cu	170	17
Ti	21.4	3
Si	not determined	-

The quantitative analysis shows a silver content with an average of 0.94 wt % and a standard deviation of 0.09 %. Among the other elements 0.87 wt % of iron is determined. Lower concentrations are detected for lead, calcium, manganese, and copper. Silicon was not quantitatively determined by ICP-OES.

The sample was also subjected to XRD analysis to identify the form of the previously identified elements and, eventually, other phases. Figure 3 shows the XRD patterns, more in detail, the presence of metallic silver was confirmed by the peaks identified in blue; the intensity of these peaks, higher than all the others, highlights how this metal is the most present in the investigated materials. Regarding the other elements, a manganese silicate hydrate phase and iron oxide were identified. Moreover, as shown by the slight hump around 15-16 degrees, there is an amorphous phase, probably quartz.

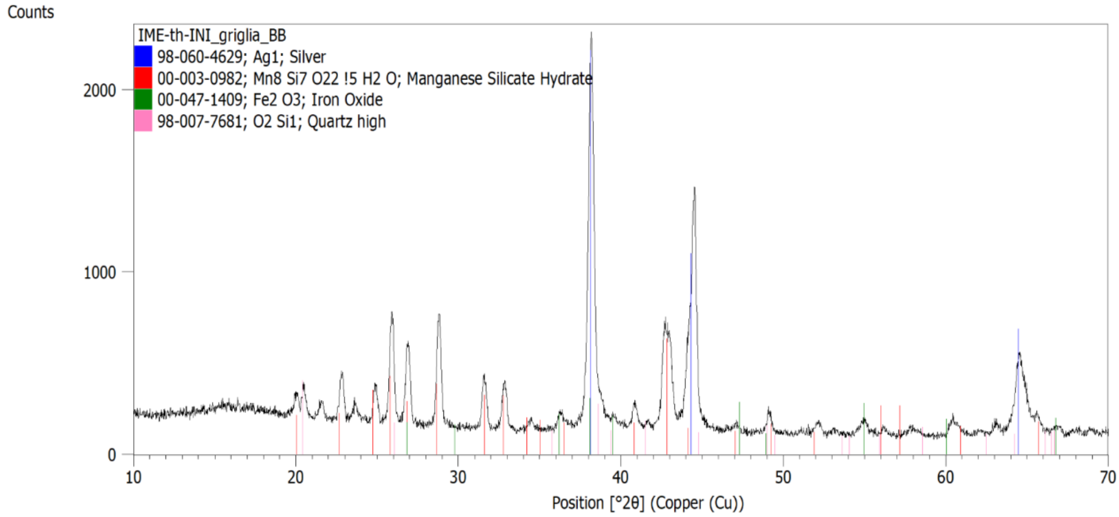


Figure 3: XRD pattern of thermoformed PC - IMSE

In addition, XRD analysis could be useful to evaluate if the hydrometallurgical treatment for the silver recovery can affect the polymeric substrate and the other phases. For this purpose, this spectrum will be compared with the one on the solid residue after the silver recycling process.

The FTIR analysis was carried out to identify the different types of polymers on the sample. In Figure 4 are shown the spectra both for the black graphic area (red curve) and for the silver ink area (purple curve). The FTIR analysis conducted on the black part found matches with the following polymers: polymethylmethacrylate, polymethacrylate, calcium phosphate and polyethylacrylate. Regarding the silver ink area instead, in addition to the same polymers, an alkyd resin has also been identified.
In any case, the values of the matches obtained by the library are low (around 35 %) because of the contribution of different polymer additives. The polycarbonate substrate that is present as a base layer, as reported by the TNO - Holst Centre, has not been identified.

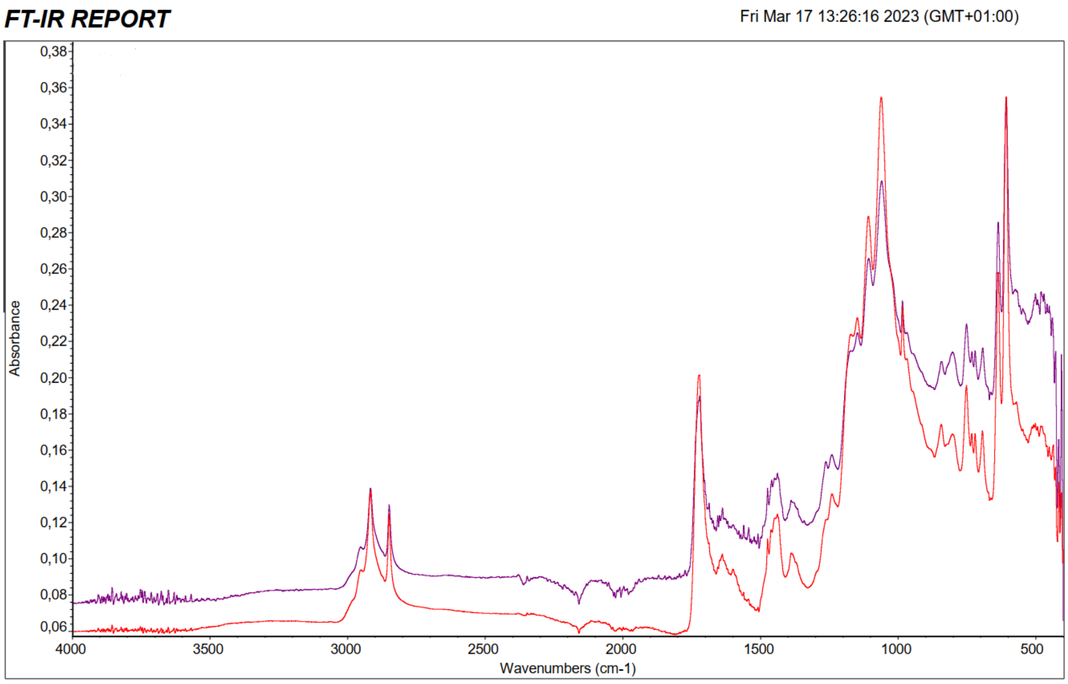


Figure 4: FTIR analysis on thermoformed PC – IMSE. The purple curve is related to the silver ink area, the red curve is related to the black graphic ink area.

3.1.2 Sample 2 – full silver area IMSE

Full silver area IMSE samples are composed of a plastic substrate and silver ink. Silver is in the surface, directly accessible for the recycling operations. The weight of each sample is in the range of 30 – 35 g for a sample size of 35x26 cm. Figure 5 shows the photographic aspect of the sample.

Figure 5: Photographic aspect of full silver area IMSE

Qualitative and quantitative ICP-OES analyses were carried out. The metal fraction of the sample was dissolved by a chemical attack by nitric acid. Qualitative and quantitative analyses have been performed on the solutions obtained by the chemical attack with the use of ICP-OES. A screening allowed to identify the most present elements and then the concentration was measured in the leach liquor to calculate the sample composition. Qualitative analyses showed that the main elements were present in the following order from most to least present: Ag, Ca, Pb, Fe, and Si; traces of Ba, Ti, Cu, and Mn. ICP-OES quantitative results and the standard deviation are reported in Table 3.

Table 3: Quantitative characterization of full silver area IMSE (ICP-OES analysis)

Thermoformed-PC sample: quantitative analysis		
element	**concentration wt %**	**standard deviation wt %**
Ag	7.417	5.883
Pb	0.122	0.012
element	**concentration g/t**	**standard deviation g/t**
Ca	632	59
Fe	407	43
Ti	128	17
Cu	71	7
Mn	< 5	-
Si	not determined	-

The concentrations are related to the sample received, also considering the transparent frame. In the transparent frame, only calcium was detected. The quantitative analysis shows a silver content with an average of 7.42 wt % and a standard deviation of 5.88 %. The standard deviation is very high as there is a great variability in the percentage of silver from sample to sample. Among the other elements 0.12 wt % of lead was determined and relevant concentration of calcium and iron. In addition, low concentrations titanium and copper were detected, 128 g/t and 71 g/t, respectively. Silicon was not quantitatively determined by ICP-OES.

3.1.3 Sample 3 – elongated IMSE

Elongated IMSE samples are composed of a polymeric substrate, different types of printed layers (with and black graphic ink) and silver ink that is bonded with a polymer additive. Silver is in the surface, directly accessible for the recycling operations. In addition, on the surface are located also several small LEDs. Figure 6 shows the photographic aspect of the sample.

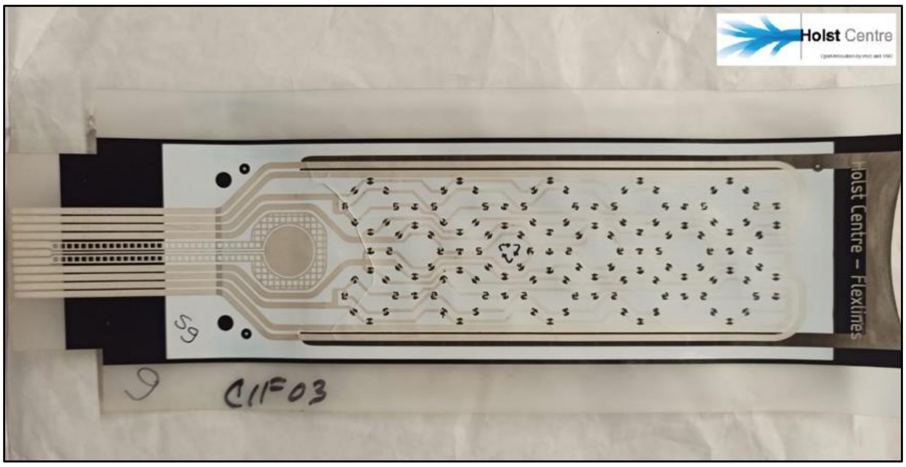


Figure 6: Photographic aspect of elongated IME with small LEDs on the surface

The weight of each sample is in the range of 7 – 8 g for a sample size of 27x10 cm. Firstly, a qualitative XRF analysis was carried out in the silver ink area as shown in Figure7.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101003587

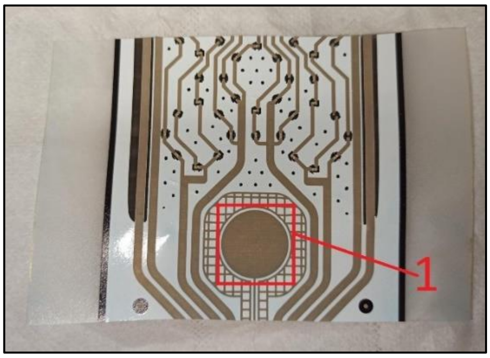


Figure 7: Map of performed XRF analysis

The analysis was carried out by cutting the piece of the sample according to the area marked on the previous figure. It was possible to obtain a semi-quantitative analysis using the internal data libraries in the processing software. XRF analysis allowed to detect both metal fraction and the other fractions (plastics, organic compounds, etc.), the results are shown in Table 4.

Table 4: Semi-quantitative characterization of elongated IMSE (XRF analysis)

Silver ink (area 1 in Figure 7)	
Element	**concentration wt %**
K	1.160
Ag	0.622
Ti	0.265
Si	0.078
Fe	0.061
Cl	0.012
Mn	0.010

Based on the XRF semi-quantitative results, potassium, silver, and titanium are the element most present in the investigated area of the sample. A concentration of less than 0.01 % was determined for the elements not reported in the table.

In addition, both qualitative and quantitative ICP-OES analyses were carried out. The metal fraction of the sample was dissolved by a double step chemical attack: firstly by nitric acid and then by aqua regia (HNO_3 : HCl 1:3 v/v). Qualitative and quantitative analyses have been performed on the solutions obtained by the chemical attack with the use of ICP-OES. A screening allowed to identify the most present elements and then the concentration was measured in the leach liquor to calculate the sample composition. Qualitative analyses showed that the main element was Ag and have also been detected to a lesser extent, Fe, Mn, Ca, Cu, and Si. ICP-OES quantitative results and their standard deviations are reported in Table 5.

Table 5: Quantitative characterization of elongated IMSE (ICP-OES analysis)

Thermoformed-PC sample: quantitative analysis		
element	**concentration wt %**	**standard deviation wt %**
Ag	3.021	0.205
Fe	0.091	0.014
element	**concentration g/t**	**standard deviation g/t**
Cu	369	65

Ti	319	34
Mn	131	42
Pb	96	27
Ca	88	15

The quantitative analysis shows a silver content with an average of 3.02 wt % and a standard deviation of 0.09 %. Among the other elements 0.091 wt % of iron was determined and relevant concentration of copper and titanium were 369 g/t and 319 g/t, respectively. In addition, lower concentrations of manganese, lead, and calcium were detected. Silicon was not quantitatively determined by ICP-OES.

3.2. Surface-Mount Devices

This section reports a characterization of the metal fraction related to different electronic components on the surface of IMSE samples. In particular, the lighting devices located on the Elongated IMSE sample and some electronic components of coffee machines were characterized.

3.2.1 LEDs on elongated IMSE

The small LEDs were manually removed from the surface of the board, then they were manually crushed and subjected to a chemical attack to dissolve the metal fraction. Firstly, a qualitative screening by ICP-OES was performed in the obtained solution to identify the most present elements. Then, based on these results, the elements on which to carry out quantitative ICP-OES analysis were selected. In Table 6 is shown the photographic aspect of LEDs, their weight, the elements detected by the qualitative screening, and the quantitative analysis results.

Table 6: Qualitative and quantitative analysis of LEDs on elongated IMSE sample (ICP-OES)

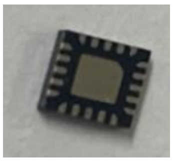
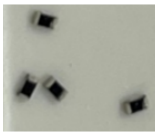
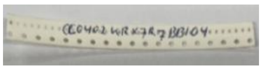
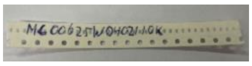
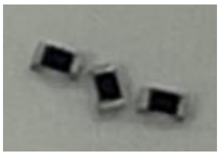
LEDs chemical characterization					
photographic aspect (IMSE)	photographic aspect (LEDs)	LED weight, mg	qualitative analysis	quantitative analysis	
				wt %	g/t
		0.43	Cu, Fe, Ni, Ag, Sn, Nd, Au, Pd, Ga, Ti	Cu 17.4 Fe 16.1 Ni 7.25 Ag 5.07 Sn 2.39 Nd 1.54 Au 1.13	Pd 128

The different forms in which the determined elements are present in the LED are not unknown.

3.2.2 Coffee machine components

Different types of electronic components (resistors, capacitors, chips, etc..) from coffee machine devices were characterized to determine the most present elements. These components were provided by TNO-Holst Center and were subjected to a chemical attack to dissolve the metal fraction. Firstly, a qualitative screening by ICP-OES was performed in the obtained solution to identify the most present elements. Then, based on these results, the elements on which to carry out quantitative ICP-OES analysis were selected. In Table 7 are shown the pictures of the components and are reported their weight and the results of qualitative and quantitative analyses.

Table 7: Qualitative and quantitative analysis of coffee machine components (ICP-OES)

	Coffee machine electronic components				
code	photographic aspect	weight of each component, mg	qualitative analysis	quantitative analysis	
AT420T2120-MMHR	 	21	Cu, Ni, Ag, Pd, Au, Fe, Ba, Ca, Si, Zn	wt %	g/t
				Cu 51.0 Ni 1.14 Ag 0.32 Pd 0.16	Au 907 Fe 690
SK6812-4020	 	22.8	Cu, Fe, Ag, Ni, Au, Nd, Sn, Zn, Sr, Pd	wt. %	g/t
				Cu 30.3 Fe 0.77 Ag 0.39 Ni 0.18	Au 676 Nd 668 Sn 624 Pd 54
RC0402FR-0797KL	 	0.82	Ni, Sn, Fe, Nd, Ag, Cu, Pd, Au, Sb, Sr, Zn	wt. %	g/t
				Ni 4.56 Sn 2.72 Fe 2.02 Nd 1.94 Ag 1.64 Cu 1.60	Pd 333 Au 247
CC0402KRX7R7BB104	 	1.50	Ni, Cu, Sn, Nd, Fe, Ag, Mn, Rb, Ti, Y, Zn, Zr, Au, PD	wt. %	g/t
				Ni 16.0 Cu 6.38 Sn 3.43 Nd 1.52	Fe 905 Ag 155 Au 25 Pd 19
MC0062JW0402110K	 	1.43	Ni, Sn, Cu, Ag, Nd, Fe, Pd, Au	wt. %	g/t
				Ni 2.98 Sn 2.43 Cu 1.50 Ag 0.74 Nd 0.51 Fe 0.33	Pd 149 Au 57

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101003587

4. Recycling process optimization

Based on the previous activities already reported in D5.3 the hydrometallurgical process developed for the recovery of silver from IMSE includes a dissolution phase conducted with a thiourea leaching system and a silver recovery phase from the solution by electrodeposition. In this section the results obtained about the recycling process optimization are described. The objectives were to reduce the chemicals consumption and the production of wastewater to obtain a MLD (minimum liquid discharge) process.

4.1. First scenario

The recycling process tests described in this section were carried out on the thermoformed PC sample; their characterization is reported in the 3.1 section.

The leaching operation was carried out through a double stage since, from previous tests, it was observed that a single step does not allow to achieve a satisfactory recovery of silver. The two leaching steps were carried out under the same conditions, thus using a fresh solution for the second. The leaching operations occurred with the following chemicals and concentrations: thiourea 20 g/L, sulfuric acid 0.2 mol/L, and Fe^{3+} 6 g/L. For each step of leaching, the time of reaction was fixed at 1 hour, at room temperature, without any agitation. However, agitation was necessary to prepare the leaching solution before starting contact with the solid.

Dissolution of silver occurs thanks to the combined action of thiourea, which acts as a complex agent, and ferric sulphate (Fe^{3+}) as an oxidant. The acidic environment and, more in detail, a pH value of about 1 is maintained by a low concentration of sulfuric acid that guarantees the conditions of maximum solubility for iron.

The following chemical reaction occurs during the leaching operations:

$$Ag + 3CS(NH_2)_2 + Fe^{3+} \rightarrow Ag\,[CS(NH_2)_2]_3^{+} + Fe^{2+} \qquad \text{(equation 1)}$$

$$2CS(NH_2)_2 + 2Fe^{3+} \rightarrow (SCNH_3)_2 + 2Fe^{2+} + 2H^{+} \qquad \text{(equation 2)}$$

$$(SCN_2H_3)_2 \rightarrow CS(NH_2)_2 + NH_2CN + S \qquad \text{(equation 3)}$$

Figure 8 shows a picture of the leaching operation. To ensure that at least the silver ink side of the solid is immersed in the leaching solution, the test was conducted at a solid concentration of 5 % w/v.

Figure 8: Thermoformed PC sample during the leaching operation

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101003587

The obtained results are reported in Table 8.

Table 8: Silver leaching results for the thermoformed PC sample, initial scenario

Leaching step	Volume, mL	Ag concentration, mg/L	Ag dissolution yield, %	Cumulative Ag dissolution yield, %
1st leaching	421	218.3	71.4	71.4
2nd leaching	421	60.4	19.8	91.2

The results obtained show that after 2 steps of leaching a high cumulative silver extraction yield of 91.2 % can be achieved.

Then, silver was recovered from the solution by electrodeposition for two hours, with constant stirring of 100 rpm and voltage of 1.2 V. The latter allowed a working current density of about 50 A/m^2, which is optimal for silver deposition from the literature analysis [1]. Two cylindrical electrodes were used: the graphite anode and the copper cathode. Using copper allows to directly recover of the silver powder in its metal form and avoids an energy-consuming subsequent phase of thermal refining that would be necessary if a silver oxide was recovered. During the electrodeposition, the following reactions occur:

cathode: $Ag(CS(NH_2)_2)_3^+ + 3e^- \rightarrow Ag^0 + 3(CS(NH_2)_2)$ (equation 4)

$3FDS + 3H^+ + 3e^- \rightarrow 3CS(NH_2)_2$ (equation 5)

anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (equation 6)

Based on the chemical reaction 5, formamide disulfide is decomposed into thiourea; therefore, a partial regeneration of thiourea could be expected.

In Table 9, the electrodeposition results in terms of silver recovery and energetic consumption are reported. The operation was monitored in time by making withdrawals every half hour.

Table 9: Recovery of silver from the leach liquor solutions by electrodeposition

Time, h	Current, mA	Ag concentration, mg/L	Ag recovery, %	current efficiency, %	energetic consumption (kWh/kg)
0.0	39	139.2	0.0	0.0	0.0
0.5	43	93.8	32.6	11.8	5.1
1.0	52	60.8	56.3	11.0	3.2
1.5	57	36.1	74.1	10.2	2.6
2.0	60	15.6	88.8	8.8	2.3

The results showed that almost 90 % of silver was recovered from the solution with an average energetic consumption of 3.3 kWh/kg. Current efficiency was calculated by the ratio between the silver electric charge and the total transferred electric charge during the electrodeposition process. By calculating the current efficiency value, it is possible to know the percentage of the electric charges used for the silver recovery. It depends on the silver concentration and on the impurities of the leach liquor solution. Current efficiencies were around 10 %, similar values with respect to those reported in the available scientific literature.

In Figure 9, the current efficiency as a function of the silver recovery is reported during the time of the electrodeposition. The intersection of the two curves indicates the optimal point at which the operation could be stopped. In fact, for higher times, excess energy consumption would not justify further recovery. This information can be considered for a process scale-up.

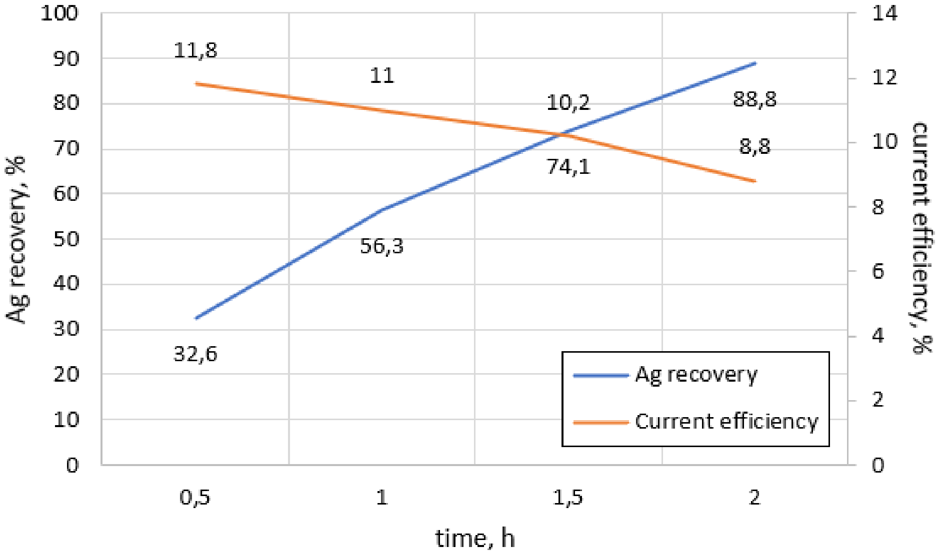


Figure 9: Silver recovery vs current efficiency during the Ag electrodeposition

The silver powder was manually recovered from the copper cathode and then subjected to a chemical attack to determine the silver grade and the impurities. ICP-OES quantitative analyses were performed on the obtained solution, the results were reported in Table 10. The results of silver powder composition are an average of different electrodeposition tests.

Table 10: Composition of the obtained silver powder

Silver powder	Ag	Cu	Fe	other (non- metallic fraction)
concentration, wt. %	47.4	5.2	2.2	45.2
std deviation	15.2	2.1	1.8	-

A silver grade of 47.4 wt. % was obtained in the powder, a high standard deviation was calculated, in fact in some tests in some tests a purity even higher than 70 % was obtained. Iron and copper have been identified as metallic impurities in the silver powder, respectively, in concentrations equal to 5.2 wt. % and 2.2 wt. %. Copper impurities may be due to scraping the copper cathode during the manual powder recovery phase, especially because copper is not present in the solution subjected to electrodeposition. The impurities related to the organic phases are due to compounds resulting from the thiourea degradation. Considering that the organic phase can be easily removed with a thermal treatment, based on the results reported in Table 9, a silver purity of 86.5 wt. % would be achieved.

Other samples of powders obtained from the electrodeposition were subject to a 600 °C thermal treatment to remove the organic phases and evaluate only the purity of the metal fraction. A silver grade of 84 wt. % was determined, and copper and iron impurities were confirmed. In addition, an XRD analysis was performed on the powder to evaluate the silver form. The obtained spectrum is shown in Figure 10.

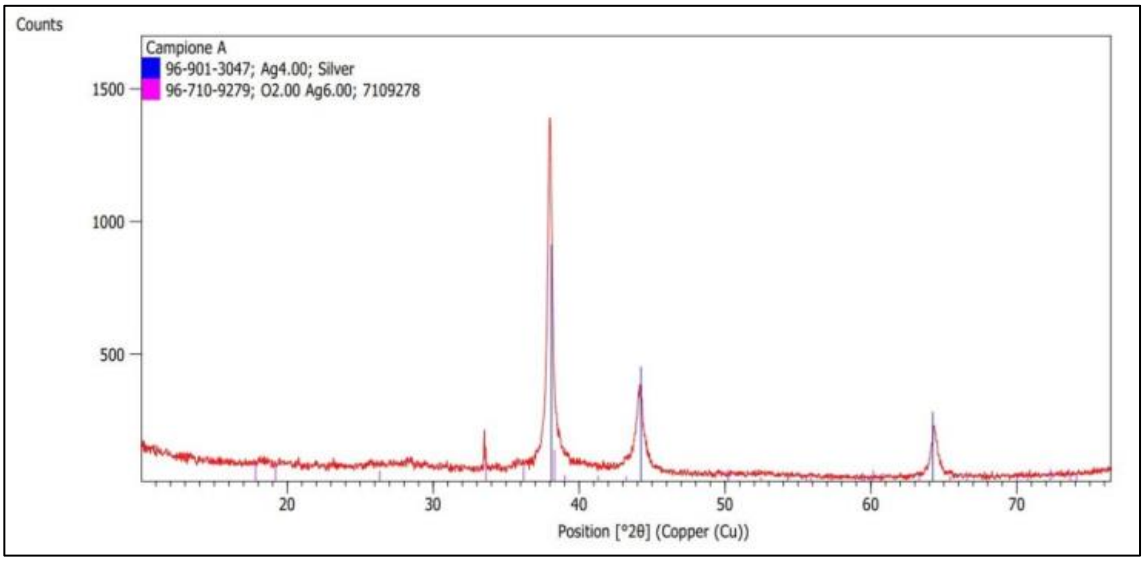


Figure 10: XRD pattern of the silver powder obtained by electrodeposition

The spectrum elaboration has shown the presence of peaks related to metallic silver, which however is also present in a less evident way even in the form of oxide.

The process scheme for silver process recycling considering the initial scenario is graphically summarized in Figure 11.

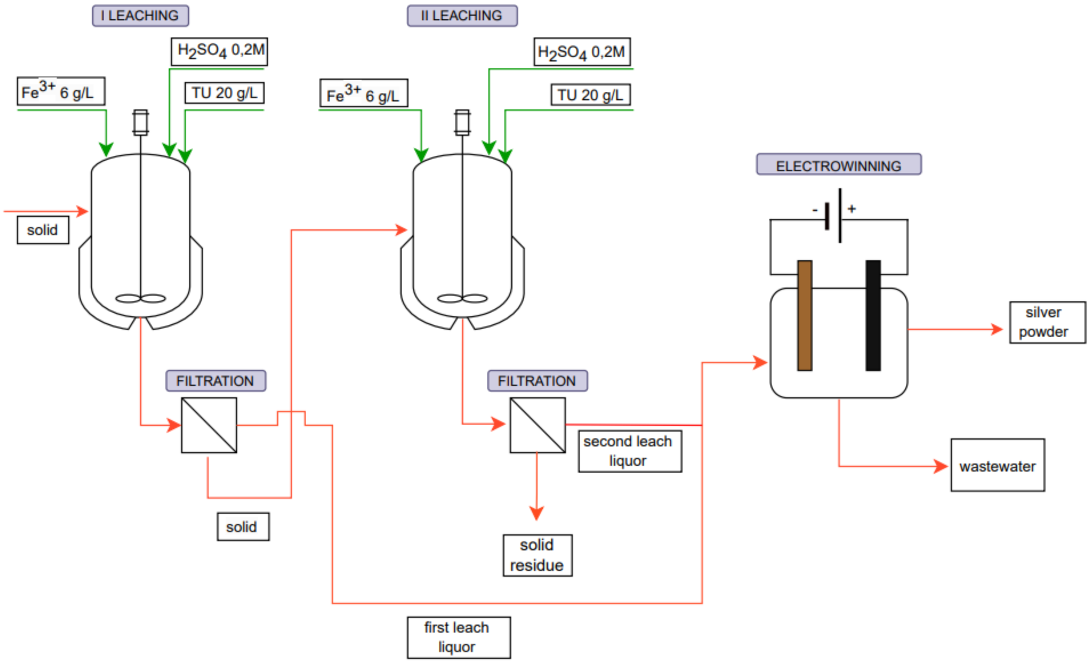


Figure 11: Silver recycling process scheme considering the initial scenario

4.2. Second scenario: recycling of the solution in the second step of leaching

The present section includes the tests to optimize the developed process aimed at reducing chemical consumption and wastewater production.

The aim was to evaluate the reuse of the leach liquor solution, obtained from the first step, to carry out the second step of leaching on the same solid. This method results in a halving of the water introduced in the process, and therefore obviously also, the amount of wastewater generated is reduced. To ensure that the leaching solution in the second step still allows it to be efficient and guarantees a moderate yield of silver dissolution, a make-up of chemicals is necessary according to the scheme reported in Figure 12.

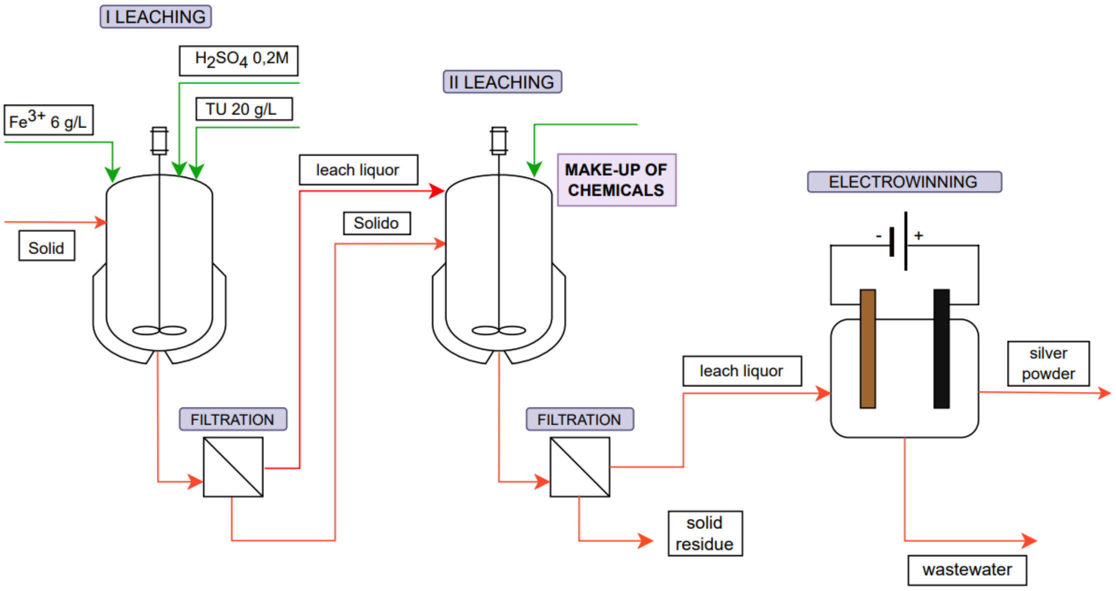


Figure 12: Silver recycling process scheme with the reuse of the solution for the 2nd leaching

About the necessary amount of each chemical for the second step of leaching: thiourea was added based on the results obtained by the titration, sulfuric acid based on the pH value and, to identify the quantity of Fe^3 to be refreshed different tests in the range 0 - 6 g/L have been carried out. Therefore, the first leaching operation was carried out according to the already identified operative conditions. Then, thiourea was titled by an iodometric method in the leach liquor solution obtained from the first leaching. The obtained result was 14.6 g/L; considering that the initial concentration was 20 g/L, the determined consumption of thiourea was 5.4 g/L, which corresponds to the quantity to be refreshed for the second leaching stage. Sulfuric acid was not readjusted since the pH was still around 1. The following tests were performed to evaluate the necessity to refresh the Fe^{3+}: no addition, 3 g/L make-up, and 6 g/L make-up; the last two tests correspond to the replenishment of 50 % and 100 %, respectively.

In Table 11, the replenishment of chemicals and the obtained Ag dissolution have been reported. Only the factor of Fe^{3+} was changed to evaluate its effect on the 2nd step of leaching, while the replenishment of thiourea and sulfuric acid was the same for all the tests. The tests have been performed on different samples of IMSE. The obtained silver dissolution of the first step was in the range of 60.0 – 68.7 % as a function of the test, with a standard deviation of 3.6 %.

Table 11: Effect of Fe^{3+} replenishment on the Ag dissolution during the 2nd step of leaching

Test number	Replenishment of chemicals for the 2nd step of leaching			Ag dissolution, %	
	Thiourea g/L	H_2SO_4 mol/L	Fe^{3+} g/L	1st step	2nd step (cumulative)
1	5.4	0.0	0.0	60.0	65.3
2	5.4	0.0	3.0	64.5	71.3
3	5.4	0.0	6.0	67.2	85.1

Based on the cumulative Ag dissolution obtained after the second step of leaching, it is possible to observe the necessity of a total replenishment of Fe^{3+}, which is the oxidant agent of the reaction and is consistent that it is consumed during the first leaching step. The variation of the increment as a function of the amount of oxidizing agent added is above variability due to the replicability of the tests. The results are also shown in Figure 13.

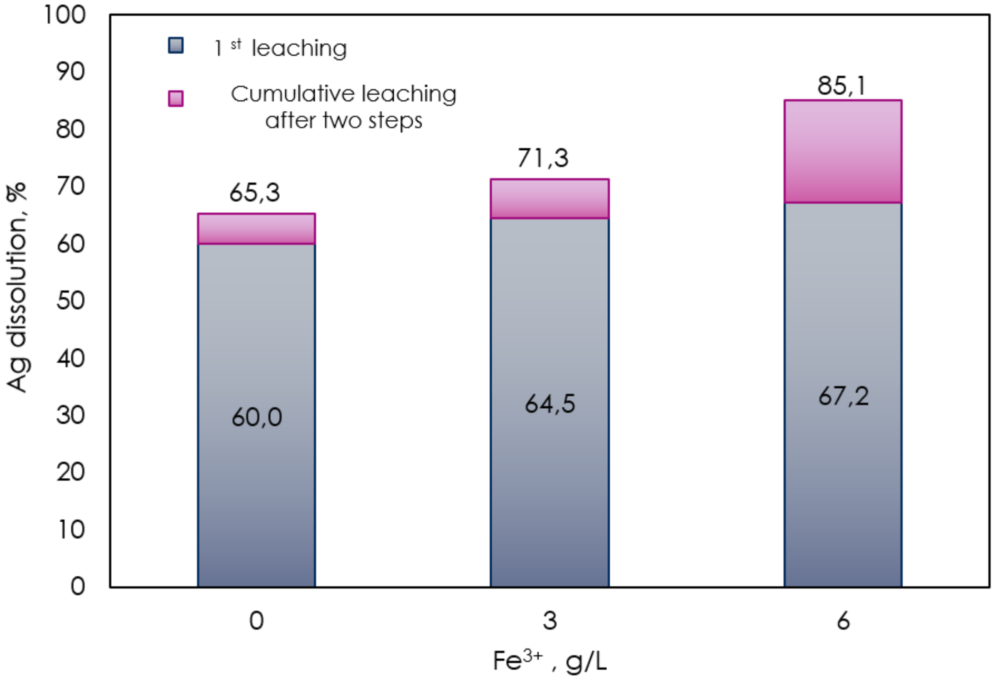


Figure 13: Ag dissolution as a function of second step Fe^{3+} replenishment

Therefore, based on these tests was deducted that it is necessary to add all the amount of Fe^{3+} to carry out the second leaching step. In addition, for each test, the electrodeposition was performed to recover the silver from the solution and to evaluate if the Fe^{3+} causes an effect on the electrodeposition. Similar silver recoveries, current efficiencies, and energetic consumption are obtained for all the tests and compared with the ones obtained by performing the leaching with fresh reagent according to the scheme shown in Figure 11. So, no effect of the addition of Fe^{3+} was observed during the electrodeposition.

Then, a test replication of the two steps leaching with the make-up of chemicals and the recovery of silver by electrodeposition was carried out. The operative conditions and the obtained results are summarized in Table 12. Solid concentration was 5 wt %.

Table 12: Chemicals concentration and results for the recycling of the solution in the 2nd step

chemical	1st leaching	2nd leaching	Results	
Thiourea g/L	20.0	5.4	1st Ag dissolution, %	65.5
Sulfuric acid mol/L	0.2	0.0	Cumulative Ag dissolution, %	88.2
Fe^{3+} g/L	6.0	6.0	Ag recovery after EW, %	85.7

The replicated test confirmed that after two steps of leaching with the reuse of the solution with a make-up of chemicals, an overall silver dissolution of 88.2 % can be achieved. Therefore, similar dissolution yields respect to the one achieved with the initial scenario but ensures a saving of chemicals and reducing wastewater. More in detail, the amount of leaching solution at the inlet is halved, the consumption of thiourea is reduced by almost 40 %, and the sulphuric acid is halved. The consumption of ferric sulphate (Fe^{3+}) remains the same.

The described scenario for the leaching operations does not interfere with the recovery of silver from electrodeposition. In fact, 85.7 % of recovery was achieved after 2 hours, current efficiencies around 10 %, and energetic consumption of 4.2 kWh/kg.

4.3. Third scenario: recycling of the solution after Ag-EW for new cycles

This section provides a description of the tests carried out to evaluate the reuse of the final solution from which silver was recovered for new treatment cycles.

After silver electrowinning, the leach solution is not sent to wastewater treatment but is used for the treatment of a new solid after appropriate replenishment of chemicals (Figure 14). This approach not only saves chemicals but also significantly decreases the production of wastewater, according to MLD. The process was studied for a total of three cycles.

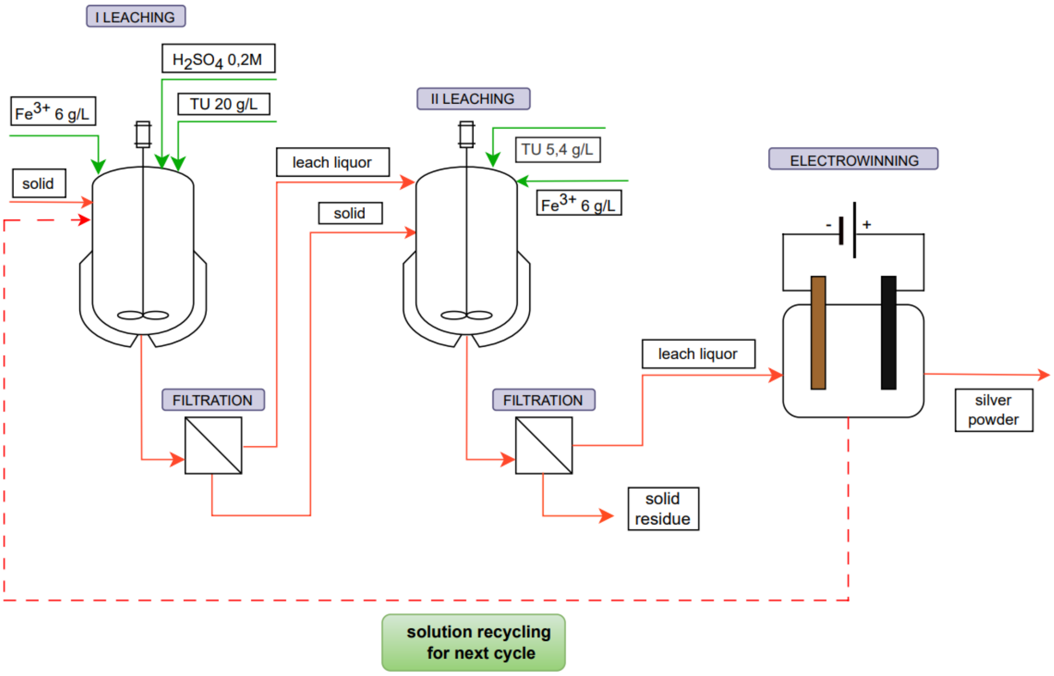


Figure 14: Silver recycling process scheme with the reuse of the solution for the next cycle

To perform the two steps of leaching the operative conditions were those already identified by the previous tests. Thiourea concentration was titled after the second leaching and was observed an average concentration of 18 g/L. Based on simplified following chemical reactions, a partial regeneration of thiourea occurs during the silver electrowinning.

$Ag(TU)^{3+} + 3e^- \rightarrow Ag^0 + 3TU$ (equation 7)

$3FDS + 3H^+ + 3e^- \rightarrow 3TU$ (equation 8)

where TU is $CS(NH_2)_2$

After recovering silver by electrowinning, the discharged solution was titled again, and the thiourea concentration was 19 g/L. Therefore, the experimental results confirmed a slight regeneration of thiourea.

Based on this result, the first step of the new cycle was performed by adding the following chemicals to the recycled solution: thiourea 1 g/L, Fe^{3+} 6 g/L. No addition of sulfuric was made. With respect to the first leaching of the first cycle, only 5 % of thiourea was necessary. The obtained results are reported in Table 13.

Table 13: Chemicals concentration and results for the recycling of the solution in the 2nd step

Cycle number	1st step Ag dissolution, %	Cumulative Ag dissolution, %	EW: Ag recovery, %
1	66.3	81.3	75.2
2	70.4	88.0	87.2
3	71.7	85.8	78.9

The results showed how the silver dissolution yields after the two steps of leaching, in the range of 81-88 %, are not affected by the number of cycle. The average value of cumulative silver dissolution was 85 %. Some replications showed that high variability in the dissolution yield was observed. Independently of the cycle, the silver dissolution can vary in the range of 70-99 %; it probably depends on the lab equipment that doesn't allow it to operate in the same condition of solid exposure.

In addition, the recycling of the solution has no effect also in the recovery of silver by electrodeposition. This aspect was checked as the increase of iron in solution, as it is added to each leaching step, could interfere with silver recovery in terms of current efficiency.

4.4. Full silver board IMSE

Tests on full silver area IMSE samples were performed to also evaluate the developed process on different types of IMSEs. This sample was selected because it has high concentrations of silver and because it is on the surface and, therefore, directly accessible. Leaching tests were carried out with multiple steps to extract all the silver contained. The configuration used is of the crossflow type with the make-up of some chemicals. In particular, the consumption of thiourea was evaluated for each step in order to be able to determine the quantity of thiourea to be reinserted in the next step. Four leaching steps were carried out. The tests were performed according to the operative conditions listed below:

a. solid concentration 10 % w/v

b. time of reaction 1 h
c. room temperature
d. thiourea 20 g/L
e. Fe^{3+} 6 g/L
f. H_2SO_4 0.2 mol/L

The obtained results are reported in Table 14.

Table 14: Silver leaching results for the full silver area IMSE samples.

Leaching step	Volume, mL	Ag concentration, mg/L	Ag dissolution yield, %	Cumulative Ag dissolution yield, %
1st leaching	300	1990	66.7	66.7
2nd leaching	290	2490	13.1	79.7
3rd leaching	285	2927	20.2	99.9
4th leaching	270	3336	0.11	100.0

A total recovery of silver was achieved after 4 leaching steps by making up the consumed thiourea. The optimal configuration consists of 3 leaching steps as the fourth step results in an increase of only 0.11% in the silver extraction yield. The introduction of this additional step involves costs that are not justified by the insignificant increase in the extraction yield. The thiourea consumption for the three leaching steps is reported in Table 15.

Table 15: Thiourea consumption for the three leaching steps.

	1st leaching	2nd leaching	3rd leaching
Thiourea consumption, g	2.832	2.545	2.065

Figure 14 shows the photographic aspect of the sample after the leaching operations.

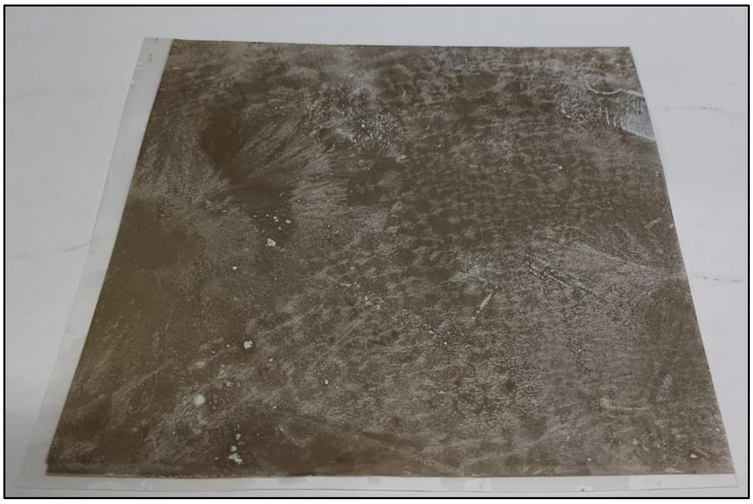


Figure 15: Full silver board IMSE after the hydrometallurgical operation to recover silver.

4.5. Elongated IMSE

Tests on elongated IMSE samples was performed to evaluate the developed process also on different type of IMSE. This sample was selected because, has the silver on the surface has the thermoformed IMSE sample, but also has several small LEDs on the same surface.

In addition to testing the process on a sample with a higher silver concentration, 3 wt %. compared to about 1 wt %. of the thermoformed samples, the objective was also to assess whether the LEDs could interfere with the extraction of silver during the leaching operations. In Figure 16, a photographic aspect of the sample with the detail of the LEDs is shown.

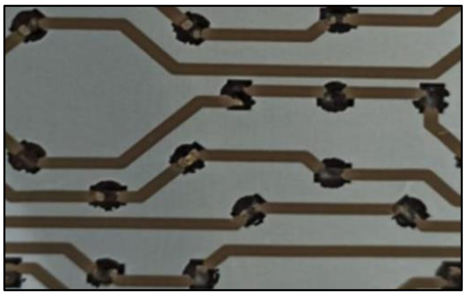


Figure 16: LEDs in the surface of the elongated IMSE sample

The tests were performed according to the operative conditions identified in section 4.2, that are listed below.

First step of leaching:

g. solid concentration 4 % w/v
h. time of reaction 1 h
i. room temperature
j. thiourea 20 g/L
k. Fe^{3+} 6 g/L
l. H_2SO_4 0.2 mol/L

Second step of leaching:

a. Solid concentration 4 % w/v
b. time of reaction 1 h
c. room temperature
d. thiourea 5 g/L
e. Fe^{3+} 6 g/L

The obtained results are reported in Table 16.

Table 16: Silver leaching results for the thermoformed PC sample, initial scenario

Leaching step	Volume, mL	Ag concentration, mg/L	Ag dissolution yield, %	Cumulative Ag dissolution yield, %
1st leaching	200	653	65.9	65.9
2nd leaching	186	767	10.7	76.6

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101003587

A total dissolution of silver of almost 77 % was achieved, the value slightly lower than 85 % obtained on the treatment of thermoformed samples may depend on an initial silver concentration of three times higher.

After the leaching operations, an XRF analysis was carried out, as shown in Figure 17. By evaluating the Ag K-alpha and L-alpha peaks, the decrease of silver content in the sample is confirmed after the two steps of leaching.

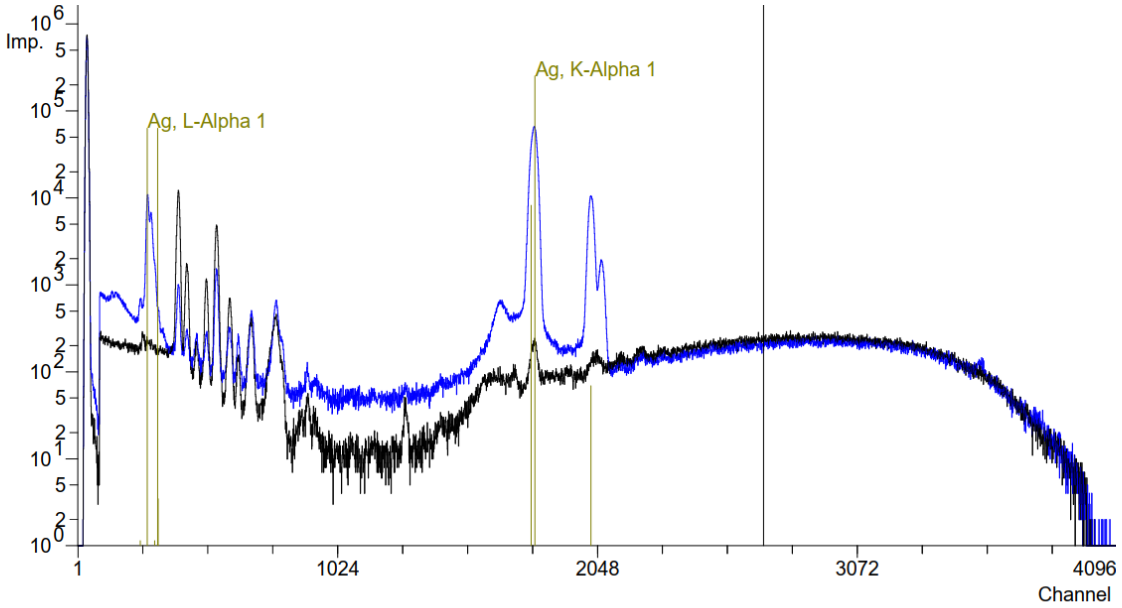


Figure 17: XRF comparison on elongated IMSE sample before (blue curve) and after leaching (black curve)

In addition, the small LEDs remains on the surface without interfering during the leaching operations. In Figure 18 is shown the sample after silver recovery; it is evident that the parts in which silver ink is present are clearer than the initial sample.

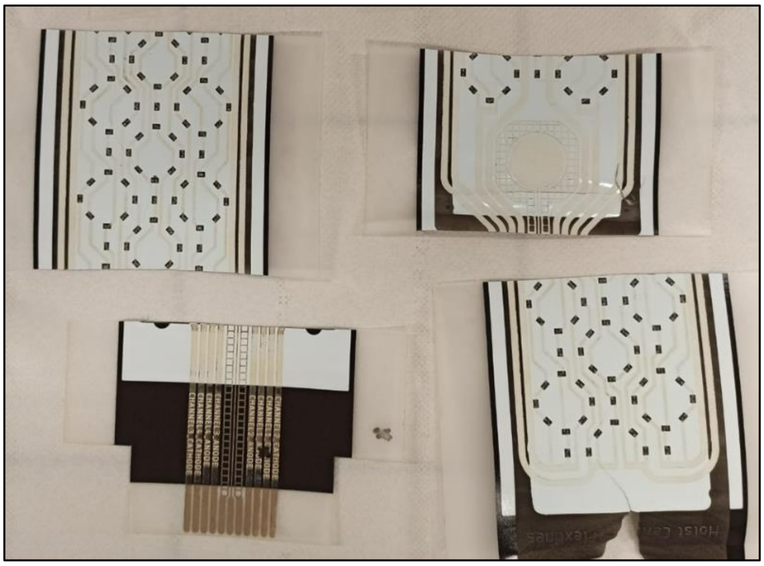


Figure 18: Photographic aspect of elongated IME sample after leaching operations

The recovery of silver from the solution was tested again with the electrodeposition at the same operative conditions studied for the other solutions. After 2 hours, 74 % of silver from the solution was recovered with a lower energetic consumption equal to 1.3 kWh/kg. This result is easily understood due to the higher concentration of silver in solution that allows to operate at a high current efficiency compared to the previous tests.

The grade of silver in the obtained powder was equal to 57.1 wt %, with the already investigated metal impurities such as iron and copper beside the organic compounds that can be easily removed after a 600 °C thermal treatment to increase the silver purity.

4.6. Process robustness assessment

The identified operative conditions for the treatment of thermoformed IMSE samples were used on a sample consisting of a mix of all types of IMSES available, always with silver directly exposed on the surface of the boards. The aim was to evaluate the process robustness by testing different types of IME. The test, in this case, was performed at 10 % of solid concentration using a conical flask; the other operative conditions were the same described in section 4.3. One or two cut-outs, depending on how visually the surfaces of the boards were made for each type, with the aim of obtaining a representative sample that simulated the treatment of all the IMSEs regardless of the type. Figure 19 shows the initial sample before the leaching operations.

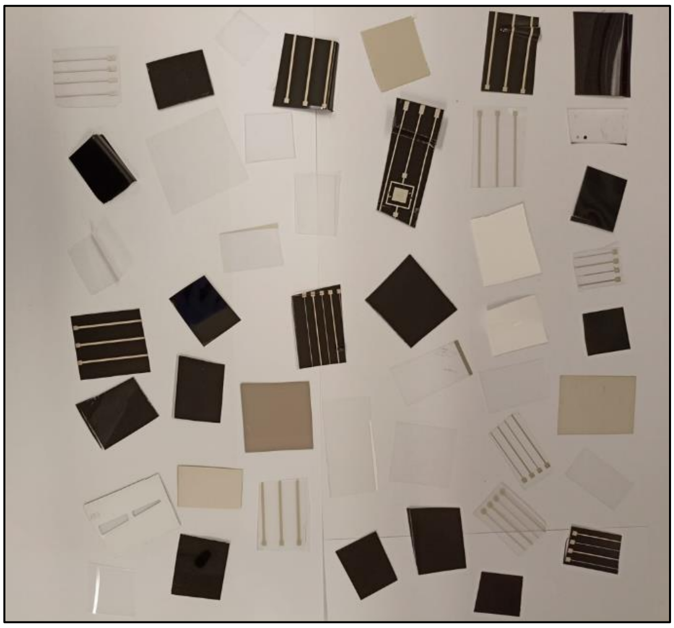


Figure 19: Photographic aspect of a mixture of IME samples before leaching operations

Two leaching steps with a make-up of chemicals were conducted. The used make-up amounts were the same as identified for the treatment of thermoformed IMSE samples. Table 17 shows the obtained results by the leaching operations. The initial weight of the samples was 10.8 g.

Table 17: Silver leaching results for the thermoformed PC sample, initial scenario

Leaching step	Volume, mL	Ag concentration, mg/L	Ag dissolution yield, %	Cumulative Ag dissolution yield, %
1st leaching	108	1246.9	65.4	65.4
2nd leaching	103	1484.3	11.9	77.3

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101003587

An overall silver yield after the two leaching stages of 77.3 % was achieved. Compared with the results obtained on the thermoformed samples, a slight reduction of silver dissolution was observed, from about 85 % to 77 %. In any case, this is a value that would largely allow the process' economic sustainability to be obtained. The decrease in the silver extraction rate depends on the higher silver content in the mixture of IMSEs, which turned out to be equal to 1.91 % with respect to 0.93 % for the thermoformed samples. To increase the yield, it would probably be necessary to determine the specific chemical consumption for this test to add what was consumed during the first leaching.

Figure 19 shows the photographic aspect of samples after the leaching operations.

Figure 19: Photographic aspect of a mixture of IME samples after two-steps of leaching

A silver content of almost 2 % in the mixture of IME samples shows how the process of recycling silver has remarkable potential in terms of profit.

5. Process analysis

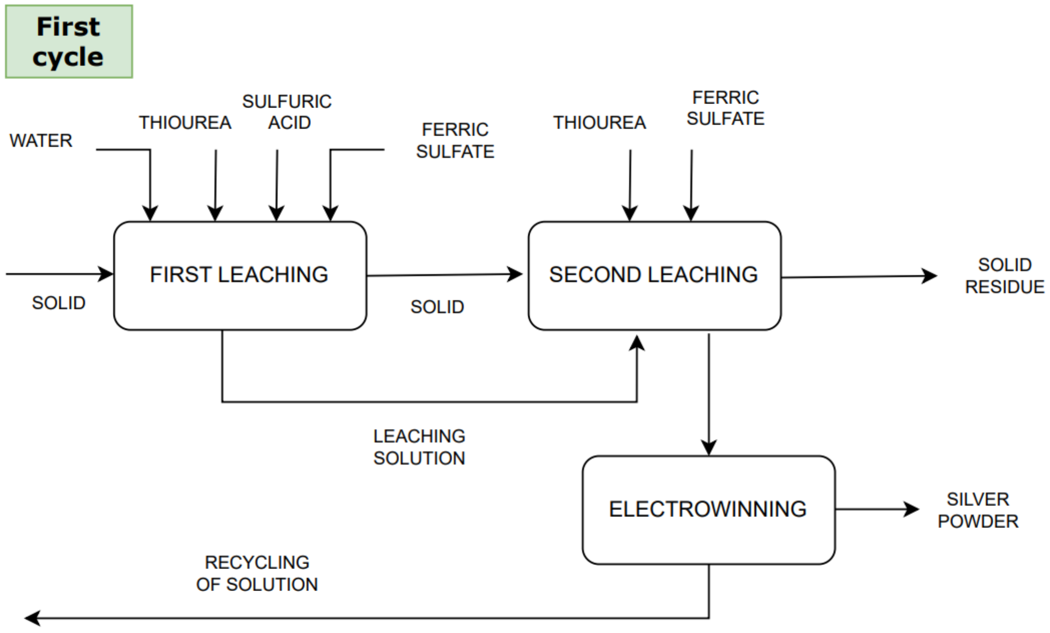
The process analysis was carried out considering the experimental results performed at laboratory scale on the thermoformed IMSE samples, according to the scheme reported in section 4.3. However, as shown by the experimental results (Section 4.4, 4.5, and 4.6) this process can also be applied to other types of IMSEs, with a slight reduction in efficiency.

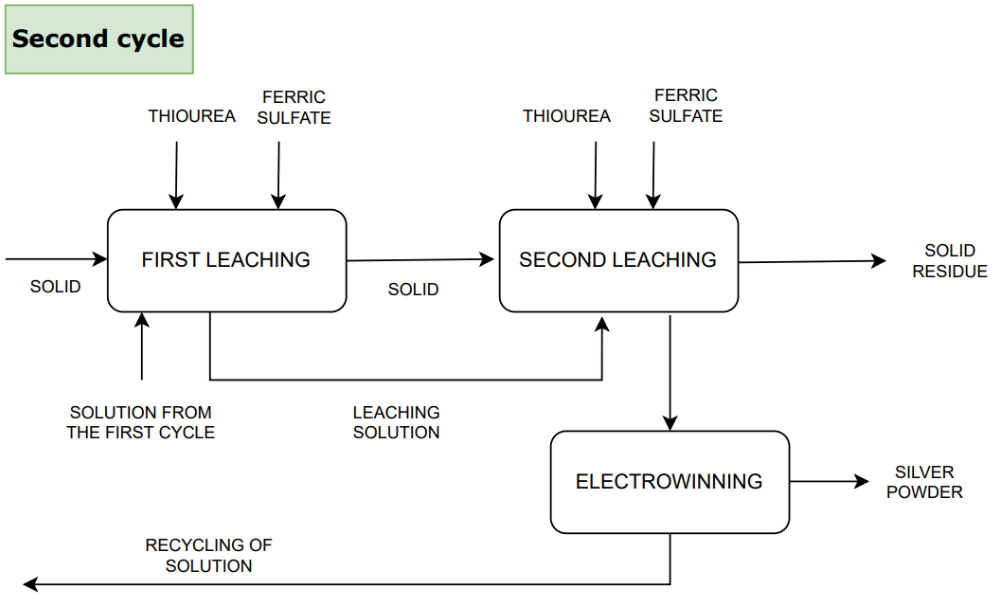
This chapter was divided into the following section: the description of the hydrometallurgical process identified flowsheet for the recycling of silver, the description of mass balances, a focus on the process outputs, and evaluations of the process feasibility by also an environmental and economic point of view.

5.1. Process flowsheet

The identified hydrometallurgical process for recycling silver from thermoformed IME was described in section 4.3. The process includes two stages of leaching for the dissolution of silver and electrowinning to recover the silver from the solution in which was dissolved. The second stage was performed on the same solid by using as a leaching solution the leach liquor obtained from the first leaching performing a make-up of chemicals based on the quantities consumed. In addition, the discharged silver solution can be recycled to carry out a second cycle on a new solid. This results in a reduction in water use and a decrease in the consumption of chemicals, also exploiting a partial regeneration of thiourea that occurs during the electrowinning operation. Solution recycling has been studied for three cycles, thus achieving a scenario that allows a significantly reduced wastewater production according to an MLD approach.

The block process scheme for each cycle of treatment is shown in Figure 20.





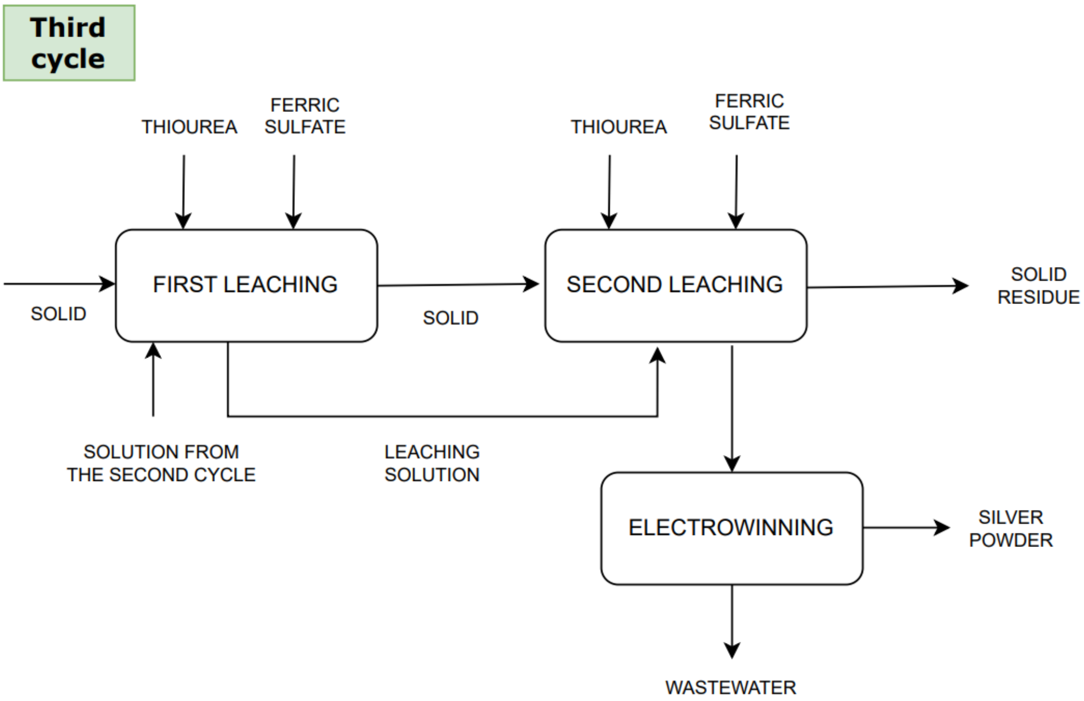


Figure 20: Block process scheme for three cycles of IMSE treatment

It is not excluded that additional cycles can also be carried out before purging for wastewater treatment. The studies should not disregard the increase in iron concentration, which could reduce energy efficiencies during electrowinning. However, keep in mind that it could also be precipitated with oxalic acid before electrowinning, should its presence worsen the efficiency of the process.

In Table 18, the results in terms of silver recoveries are reported for each step of the process.

Table 18: Summary of the obtained results in terms of silver recovery

Process step	Ag, %
First leaching	69.5
Second leaching	85.0
Electrowinning	87.5

Adopting the proposal process to thermoformed IMSE samples with a silver content of 0.93 wt %, operating at a solid concentration of 10 % w/v, a silver dissolution of 85.0 % can be achieved after two steps of leaching, calculated as the average value for the three treatment cycles. It should be noted that the recovery of silver obtained by electrowinning is closely linked to the equipment used. Generally, industrial-scale electrowinning achieves recoveries of more than 95 %.

5.2. Mass balances

Based on the experimental results, mass balances referred to the hydrometallurgical process of 1 ton of IMSE are reported in Table 19. The mass balances are calculated according to the process with three cycles of treatment with the recycling of solution and make-up of some chemicals.

Table 19: Mass balances for the treatment of 1 ton of thermoformed IMSE

Input, kg		Output, kg	
solid	1000.0	dry solid	991.2
water	3239.8	humidity	70.7
thiourea	127.8	powder from EW	14.6
ferric sulphate	441.2	wastewater	3863.2
sulfuric acid, 50 %	130.9	-	-
total	**4939.7**	total	**4939.7**

Concerning the outputs, the humidity is referred to the water that remains on the solid after separating the leach liquor solution from the solid and to the water associated with the powder recovered from the cathode after electrowinning; based on the experimental results are equal to 6.1 % and 40 %, respectively. By focusing on the dry solid quantities, you can see that almost all the solid input comes out as the output of the process; therefore, managing this solid is crucial for environmental sustainability analysis. The powder amount recovered from the cathode is not referred only to the silver but also the impurities. The silver amount in the powder is 6.9 kg, while the metallic fraction is 8.0 kg. Finally, wastewater output is 3863.2 kg with a density of 1.15 g/cm^3.

In addition, Table 20 summarizes the distribution of various elements for each process output. The most present elements in the initial sample are considered.

Table 20: Distribution of various elements in the process outputs

Process output	Ag, %	Fe, %	Cu, %	Mn, %	Ti, %	Si, %
Solid residue	15.0	9.9	30.2	25.7	44.6	100.0
EW - Silver powder	74.4	-	-	0.0	0.0	0.0
Wastewater	10.6	-	-	74.3	55.4	0.0

The table shows that silver dissolution is 85.0 %, then after electrowinning, 87.4 % is deposited on the cathode and recovered in the form of metal powder, the remaining is in the wastewater. With respect to iron and copper, their dissolution yields are 90.1 % and 69.8 %. It is impossible to establish their distribution among the silver powder and the wastewater because they are found in the recovered powder, but this may also be due to other sources. For example, iron was added in high amounts during the leaching operations, and the cathode material is of copper, and since the powder is recovered from the electrode by manually scraping the impurity could also depend on this. Manganese and titanium during the leaching operations are dissolved with a yield of 74.3 % and 55.4 %, respectively; during the electrowinning, they remain in the wastewater. Silicon, instead, was not dissolved and thus remains in the solid output.

5.3. Outputs characterization

In the present section, the following outputs were characterized to evaluate their management better:

a) solid residue
b) powders from the electrowinning
c) wastewater

The management of the solid residue, based on the high amount, is a crucial point of the developed process. The aim is to evaluate if the plastic substrate is affected by the leaching operations for silver recycling. Figure 21 shows the photographic aspect of a thermoformed IMSE sample before and after the leaching extraction.

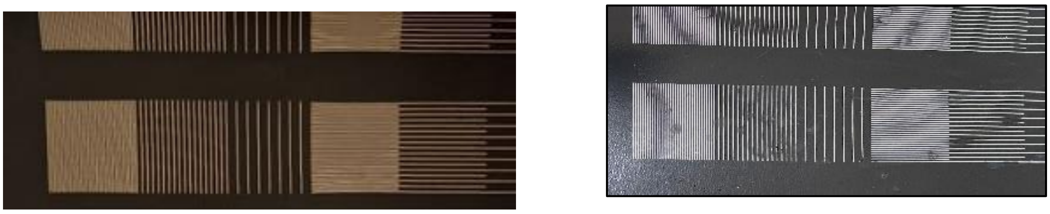


Figure 21: Photographic aspect of IMSE sample before (left side) and after leaching operations.

The figure shows how visually the silver ink's rows have become white after leaching operations. In addition, the striped part has been analysed via XRD to evaluate possible changes in the phases. The XRD pattern is shown in Figure 22.

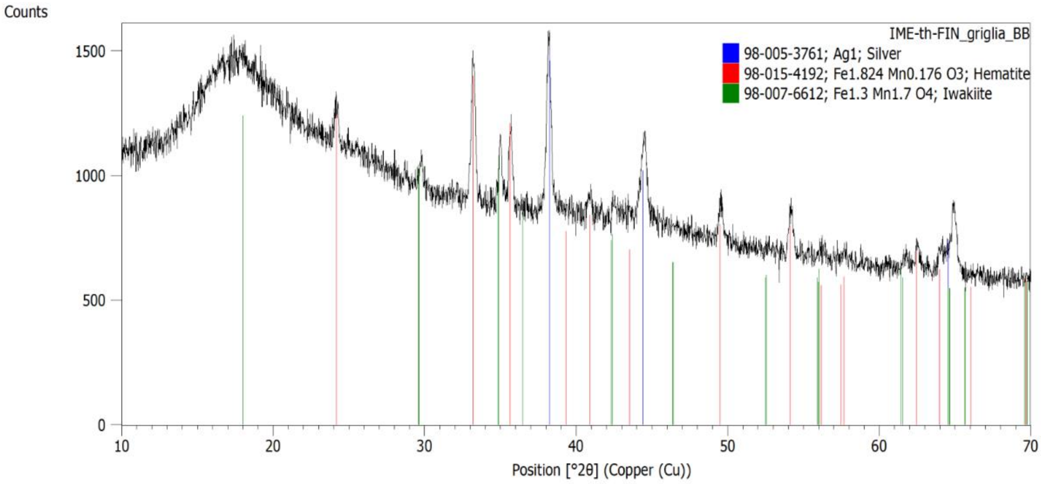


Figure 22: XRD pattern of the solid process output

The spectrum shows the presence of a hump in the range of 10-25 degrees, indicating an amorphous phase in the material. This result could be due to decreased intensity of the silver peaks since it is recovered or even a possible effect of hydrometallurgical treatment. With the aim of carrying out further evaluations on the quality of the polycarbonate substrate, some samples were sent to TNO Holst Centre.

Regarding the recovered powder from electrowinning, the grade of silver is the main aspect to evaluate the economic sustainability of the process. In Table 21, the compositions of the powder after electrodeposition and after a 600 °C thermal treatment are reported.

Table 21: Composition of the powder recovered after electrowinning.

Elements	powders wt %	After 600°C thermal treatment wt %
Silver	47.4	86.5
Copper	5.2	9.5
Iron	2.2	4.0
Non-metallic fractions (organic compounds, graphite)	45.2	0.0

First, it is necessary to consider that given the small quantities obtainable on the laboratory scale, powder composition could be affected by experimental errors. Therefore, for more assessments, it is necessary to consider the powder obtainable on a pilot scale.

Based on the lab-scale experimental results, a silver grade of 47.4 % ± 8.2 % was determined. The metallic impurities were copper and iron. Copper maybe because the powder is recovered by the copper cathode manually, and therefore, there may be contamination with some copper particles removed unintentionally from the cathode. Iron impurity, on the other hand, could be due to the contamination of the solution in contact with the powder on the cathode when the current supply ends before removing the cathode from the electrolysis cell. This could therefore be an impurity closely related to the equipment used on a lab scale. Non-metallic fraction is composed of organic compounds resulting from the degradation of thiourea that occurs during the electrowinning operation, such as free sulphur, or graphite from the anode.

The non-metallic fraction can be removed after a 600 °C thermal treatment to increase the purity of silver in the final product of the process, but also the other metallic fractions. A silver grade of 86.5 % could be theoretically obtained based on the composition of the powders; the experimental test allowed us to closely match this value, with a result of about 84 %. XRD analysis on the powder confirmed that silver is mainly in its metallic form, but from the spectrum are also visible less intense peaks of silver oxide (Figure 10), this would make the other metallic impurities would be lower. In any case, if such metallic impurities remain, given the melting point of the silver lower than that of copper and iron, thermal refining that guarantees high purity of silver could be achieved.

Wastewater composition after three cycles of IMSE treatment is reported in Table 22.

Table 22: Composition of process wastewater.

Elements	Concentration, mg/L
Fe	19682
Cu	222.7
Ti	209.5
Mn	123.1
Ag	60.59

The main element present in wastewater is iron, with a concentration of almost 20 g/L, obviously derived from the reagents used during the leaching phase; in fact, it is added as ferric sulphate at each leaching step. The other elements that compose the wastewater have concentrations lower than 250 mg/L, they derive from elements present in the initial IMSE solid that were dissolved during leaching operations.

A pH value of around 1 is measured in the wastewater, with a sulfuric acid concentration of about 0.2 mol/L, sulphates, thiourea, and formamidine disulphides are detected.

Two different routes for wastewater treatment can be conducted: the first by neutralizing the acid solution with lime hydroxide up to a pH of about 9, thus ensuring the precipitation of metals; the second one through the advanced oxidation processes like the Fenton one. In the present case, it has been hypothesized the wastewater disposal to an external company, but for the construction of a plant, it would be considered also to include a wastewater treatment section to decrease operating costs.

5.4. Economic and environmental evaluations

Economic evaluations on the silver recycling process are done based on the balance materials, calculated by experimental lab tests, and referred to a treatment of 1 ton of IMSE.

Pending a more reliable result about the silver purity of the obtained powder, which can be provided from the pilot tests, for now, a 20 % of silver value depreciation was considered for the preliminary economic analyses. In addition, beyond the sale of the silver output, the idea is also to evaluate the possibility of reusing silver as a precursor to produce silver ink to be reused to produce IMSE from the perspective of a circular economy approach.

Table 23 shows the chemical costs for the treatment of 1 ton of IMSE.

Table 23: Chemical consumptions and costs for the treatment of 1 ton of IMSE.

Chemical	Amount, kg	Cost per unit, €/kg	Cost, €
water	3239.8	0.0015	4.9
thiourea	127.8	1.00	127.8
ferric sulphate	441.2	0.30	132.4
sulfuric acid, 50 %	130.9	0.13	17.0
			282.1

The total cost of chemicals is 282.1 €. The pie chart shows the contribution of each chemical to the total cost of chemicals (Figure 23).

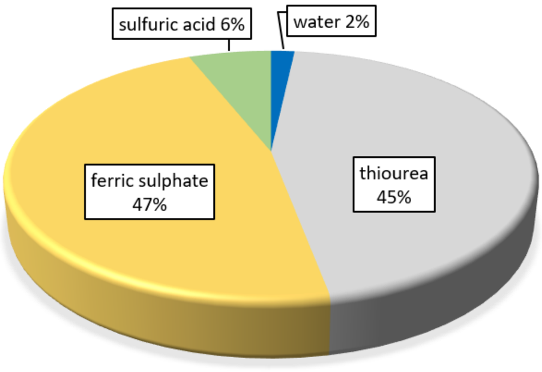


Figure 23: Contribution of each chemical on the total cost of chemicals.

It can be observed that titration of thiourea has made it possible to reduce the amount used in the process and, therefore, to significantly reduce its associated cost of carrying out the process.

Even now, the contribution of thiourea is 45%, lower than the one related to the ferric sulphate, despite the unit cost of thiourea being significantly higher.

Operative costs, OPEX (operative expenses), in addition to the cost of chemicals, also include the cost of energy consumption and the costs for the disposal of process outputs such as wastewater and solid residue.

Regarding energy consumption, a proposed process can be developed in a plant that requires the following equipment: two chemical reactors, one cartridge filter, one electrolysis cell, and three pumps, in addition to the pump for the recirculation of the solution during the electrowinning operation. It is also necessary to consider the heating of an oven for the removal of organic compounds from the powder obtained by the electrowinning operation. Then a scrubber for acid gas extraction and neutralization is necessary, so also included is the energy cost related to the gas suction from the fan and the recirculation pump for the soda bath used for neutralization. In Table 24, OPEX is reported for treating 1 ton of IMSE.

Table 24: OPEX for the treatment of 1 ton of IMSE.

Item			Cost, €/ton of IMSE
Chemicals	details are reported in Table 19		282.1
Energy consumption	kWh	€/kWh	51.5
	143	0.36	
Wastewater	m^3	€/m^3	436.8
	3.36	130	
Solid residue	kg	€/kg	-
	991.2	to be evaluated	
			770.4

The OPEX is 770.4 €/ton, even if the cost associated with the solid residue was excluded since the management of the solid residue remains crucial for a better assessment of economic and environmental sustainability. It can be observed that the highest cost is that relating to the treatment of wastewater. Therefore, for the hypothesis of realization of an industrial plant, it is suggested to introduce a section for wastewater treatment both to reduce these costs and for greater environmental sustainability because the water, once separated from the sludges, could be reused in the process according to an approach that aims at ZLD (zero-liquid-discharge) processes.

Regarding revenues, the price of silver metal must be considered. The average price in April 2023 was 24.6 $ per ounce, which is equal to 789 €/kg. To avoid setting economic sustainability on temporary situations, reference is made to the average price of the last 5 years (Figure 24).

Silver Prices - Historical Annual Data

Year	Average Closing Price	Year Open	Year High	Year Low	Year Close	Annual % Change
2023	$23.16	$23.96	$25.80	$20.01	$25.05	4.53%
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%
2019	$16.22	$15.65	$19.55	$14.32	$17.90	15.36%

Figure 24: Silver prices in the last 5 years, expresses in $/ounce. Source: Macrotrends [2]

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Last five years average price has been 21.4 $ per ounce, which is 686 € per kg.

In addition, given that on the basis of the lab-scale tests, the purity of the recovered silver is about 85 %, with impurities such as copper and iron, for the calculation of revenues, a depreciation of 20 % is assumed. The total amount of the metallic powder after 600 °C of thermal treatment is 8.00 kg, obtained from the treatment of 1 ton of IMSEs.

Based on these considerations, assuming a depreciated silver sales value of 549 €/kg, the process revenue is 4392 €/ton. Therefore, subtracting OPEX, you have a **3621.6 €/ton profit**.

For a more detailed economic analysis, once the correct capacity of an industrial plant has been identified based on how many IMSEs are present on the market, you can estimate the cost of the equipment needed for the process to define the CAPEX. In this way, assuming also a depreciation period for the investment costs, it will be possible to calculate some important economic indexes such as PBT, ROI, and NPV to concretely understand the profit margins for the process of silver recycling from IMSE.

6. Conclusions

With the aim of studying the optimization of the hydrometallurgical process for the recycling of silver from IMSE samples, the following results have been achieved:

a. Metal fraction characterization based on the different IMSE samples allowed us to determine that silver is present in its metallic form with the following contents:
    i. Thermoformed: Ag 0.93 wt %
    ii. Full silver board: Ag 7.42 wt %
    iii. Elongated board: 3.02 wt %
    iv. Mixture of all received samples: 1.91 wt %

    Concerning the other elements, the most present were silicon for all the samples and iron, mainly for the thermoformed sample in a concentration of 0.86 wt %. As regards those detected at lower concentrations were manganese, titanium, calcium, copper, and lead for full silver board samples.

b. The hydrometallurgical process includes two stages of leaching by using thiourea, ferric sulphate, and a low concentration of sulfuric acid. The recovery of silver from the leach liquor solution occurs by electrowinning on a copper cathode. For the process optimization of the leaching operations, different scenarios were studied:
    i. First scenario: two stages of leaching by performing the second step with a fresh solution on the same solid. In this case, about 91 % of silver dissolution has been achieved (section 4.1).
    ii. Second scenario: the reuse of the first leach liquor solution was studied to carry out the second step of leaching on the same solid, with a make-up of chemicals based on their consumption. The results showed a silver dissolution yield in the range of 85 % - 88 % (section 4.2).
    iii. Third scenario: starting from the previous scenario, the solution's reuse for new treatment cycles after the silver electrowinning was studied. In this case, a thiourea partial regeneration that occurs during the electrowinning was also exploited. The process was studied for three cycles. An average value of silver extraction yields of 85 % was obtained.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101003587

c. The identified hydrometallurgical process, according to the third scenario, allowed to reduce the wastewater production by about 85 % compared to the first scenario and 65 % compared to the second scenario. For this reason, the process belongs to MLD processes and thus allows it to be sustainable from an environmental point of view.

d. The energetic consumption of silver electrowinning is in the range of 3-5 kWh/kg based on the different tests, with a silver recovery after 2 hours of 87.5 %.

e. The silver powder, based on the lab-scale tests, must be subjected to a 600 °C thermal treatment to increase its purity since about 47.5 % of organic compounds are identified. After the refining, the metal composition was Ag 86.5 %, Cu 9.5 %, and Fe 4.0 % (section 5.3). Silver was mainly detected in its metallic form, but traces of silver oxide were also identified.

f. Wastewaters are mainly composed of iron (about 20 g/L); the other elements detected in concentrations lower than 250 mg/L are copper, titanium, manganese, and silver. Treatment of wastewater can be carried out by calcium hydroxide or the Fenton process.

g. Economic sustainability studies, by assuming a treatment of 1 ton of IMSEs, show that OPEX is 770.4 €/ton. Specifically, 282.1 €/ton for the chemicals, 51.5 €/ton for the energetic consumption, and 436.8 €/ton for the treatment of wastewater by considering, for now, disposal at an external company. By assuming a depreciation of silver price of 20 %, since the detected impurities, the revenue is 4392 €/ton. Therefore, the process profit is 3621.6 €/ton.

The next steps are related to confirming the silver grade of the powder based on the higher amount that could be obtained by pilot plant tests. In addition, the direct reuse of the silver powder as a precursor to producing ink would be evaluated. Another crucial point is on the management of solid residue process output, the following options will be evaluated: reuse as the substrate to produce new IMSEs, energy valorisation, and disposal. Then, the correct size of a potential industrial plant could be identified after a marker analysis aimed at estimating the amount of IMSEs available to be treated by the developed hydrometallurgical process.

Abbreviations

CAPEX	Capital Expenditure
EW	Electrowinning
FDS	Formamidine disulfide
FTIR	Fourier Transform Infrared
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IMSE	In-Mold Structural Electronics
MLD	Minimum Liquid Discharge
NPV	Net Present Value
OPEX	Operative Expenses
PBT	Pay Back Time
PC	Polycarbonate
ROI	Return of Investment
SMDs	Surface-Mount Devices
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
ZLD	Zero Liquid Discharge

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[1] T. Nawaz, S. Sengupta, C.L. Yang, Silver recovery as Ag 0 nanoparticles from ion-exchange regenerant solution using electrolysis, J. Environ. Sci. (China). 78 (2019). https://doi.org/10.1016/j.jes.2018.09.012.

[2] Macrotrends – Silver Prices 100-year historical chart https://www.macrotrends.net/1470/historical-silver-prices-100-year-chart (accessed on 01/05/2023).

D5.4: Pilot-scale reconfiguration, testing and optimization of a materials recovery process

Annex 3 – Recycling process optimization of printed circuit boards

31/05/2023 (M24)

Author: Nicolò Maria Ippolito, Francesco Vegliò, Hossein Shalchian, Marco Passadoro (UNIVAQ)

TABLE OF CONTENTS

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1. Background

Printed circuit boards (PCBs) are an essential component of any electronic waste [1]. In automotive manufacturing industries, the use of PCBs inside a car is necessary for the management of almost all the functionalities of a vehicle and the trend is drastically increased in the last decades [2]. Hence, the massive generation of end-of-life cars containing PCBs with significant amounts of valuable metals, alongside the rapid depletion of natural resources makes a driving force for recycling this kind of waste. So, their recovery allows the restoring of significant amounts of base and precious metals for production of new cars.

Various processes are used for PCB metallic content recoveries, using physical, pyrometallurgical, hydrometallurgical, and combined technologies. Pre-treatments and dismantling of the components play a significant role in upgradation and efficient metal extraction from PCBs [1]. Therefore, dismantling process can be considered as a necessary step before any other chemical treatment.

Deliverable 5.3 “Simulation and lab-scale testing of materials recovery processes” provided some information relating to the laboratory-scale treatment of numerous materials in the automotive sector using hydrometallurgical processes. The activities carried out in the ambit of Task 5.3 firstly involved a chemical characterization, also specific for each SMD. Based on the obtained results, mainly in terms of gold and copper content, but also regarding the different shapes of each component, different recycling routes were defined. Then, some components have been identified that need to be removed from the boards as they inhibit dissolution yields. Other components with high content of gold, superficially exposed, can be treated by a hydrometallurgical process to recover the metal values. The rest of the board can be subjected to another hydrometallurgical process after a preliminary physical treatment of particle size reduction.

This document, related to the activities on Task 5.4, presents a detailed analysis of the characterization of PCBs and their components, especially in dashboards, and provides process optimization for selective recovery of precious and base metal contents using two patented processes of GOLD-REC 1 (GDR1) and GOLD-REC 2 (GDR2) [3, 4].

2. Materials and methods

Various dashboards provided by partners (POLLINI and SEAT) were considered for recycling experiments in the lab scale. Each dashboard was disassembled to gain their relevant PCBs. According to different chemical composition of various components in the electric boards, some components assuming to have more content of precious metals were detached from the bords to be treated by patented process of GDR2 and the main electronic boards with remaining components were pulverized and treated by the other patented process of GDR1. These two processes were described in D5.3.

For each part of solids, leaching experiments were performed according to the above-mentioned processes of GDR1 and GDR2, and the pregnant leaching solution obtained by filtration underwent through selective metals recovery processes. Leaching efficiency and recovery percentages were calculated by analyzing solutions using ICP-OES and making mass balance to the whole process.

3. Characterization and identification of the recycling routes

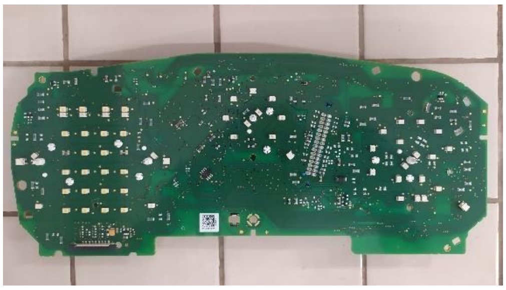
In this section, chemical characterization of detached components (for GDR2) and pulverized mixture of the main electronic boards with remaining components (for GDR1) were performed using dissolution method and the resulting solution was analyzed by ICP-OES to determine the content of the different precious and base metals of interest. Due to the rarity of each component and presence of different components on each electronic board, the total amount of each element was calculated by considering the mass of elements in each leaching solution, and the remained mass of elements in final solid residue, which was determined by chemical attack using aqua regia. So, leaching efficiency in each stage can be calculated based on the chemical analysis obtained in this manner.

3.1. Car manufacturer (SEAT - different car models)

SEAT has supplied automotive components for 3 different types of cars: SEAT 350 LEON II, SEAT 370 LEON III and SEAT IBIZA IV. As stated before, each dashboard was disassembled into its sub-components using the instructions provided by SEAT. Photographs and weight percentages were reported before in D5.3.

The dashboard of SEAT 350 LEON II with the main electronic board and its components can be seen in Table 1.

Table 1: A view of SEAT 350 LEON II dashboard and its main electronic board.

Model	Photo	
SEAT 350 LEON II		
		

As stated before, the electronic board of the dashboard disassembled into its sub-components. Some components that were suspected to have more content of precious metals were detached from the bords to be treated by GDR2 process. The rest of the board was grinded up to 2 mm as particles size to be treated by GDR1 process.

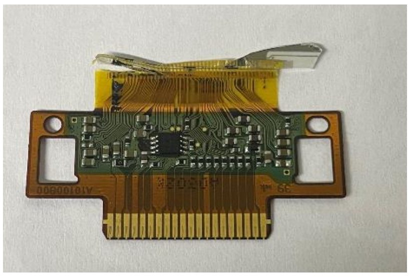
3.1.1 Powders of PCBs

PCBs' powders for the different car models were obtained after the following operations. Firstly, the components to be removed from each board were identified based on previous tests. Some of these components are removed because they inhibit the recycling rates or to be treated by a specific hydrometallurgical process. Then, the board with some residual components is subjected to a grinding up to obtain a powder with a particle size below to 2 mm.

In Table 2, a list of components that are removed before grinding and characterization is reported. Not all these components are present in all three car models.

Table 2: Components removed before grinding the board and characterize the powders.

name	photo	weight [g]	wt %
Electromagnets		11.43	5.75
Blue connector		7.32	3.68
Black connector		7.76	4.26
Display connector		0.59	0.30
Transducer		8.76	4.41
Aluminum electrolytic capacitor		2.43	1.33

Crystal oscillator		0.67	0.44
Inductors		2.02	1.11
Small PCBs connected to the display		0.54	0.27

The weight for the previous table is referred to each component, based on the different SEAT car models the components may be more than one. In SEAT Leon II there are four electromagnets, three aluminium capacitors, one transducer, one crystal oscillator, one blue connector, one display connector and one small PCBs. In SEAT Leon III are found the following components: two electromagnets, one transducer, one black connector, five aluminium capacitors, three inductors, one display connector and one small PCBs. Instead, SEAT Ibiza IV is composed of the following: two electromagnets, one transducer, one crystal oscillator, one aluminium capacitor, one blue connector and one display connector.

After removing all the components, the board with the residual components, also including the integrated circuit chips who are rich in gold, is grinded. The obtained powder has a content by weight compared to the initial PCB of about 70 %.

In Table 3, the chemical characterization of powders from SEAT Leon II is reported. The analysis was performed after chemical attack of the powder and subsequent quantitative analysis by ICP-OES.

Table 3: Powders of SEAT LEON II after removal of the above-listed components.

replications, n.	Au, g/t	Ag, g/t	Pd, g/t	Cu, %	Sn, %
1	69.6	439.4	28.5	21.5	0.68
2	112.2	339.5	32.1	22.7	1.01

3	81.2	188.6	18.5	25.5	1.28
4	63.1	223.9	14.2	13.9	1.07
average	**81.5**	**297.9**	**23.3**	**20.9**	**1.01**
std dev	21.8	114.3	8.4	4.96	0.25

Concerning with the precious elements the following concentrations are detected: Au 81.5 g/t, Ag 297.9 g/t, Pd 23.3 g/t. The most present element is copper with a concentration of 20.9 wt %, while Sn is 1.01 wt %.

The sample was also subjected to XRD analysis to identify the form of the previously identified elements and, eventually, other phases. Figure 1 shows the XRD pattern in which is evident that due to the high copper content only its peaks are well identified. Copper is present in the sample as metal. Concerning with the other elements, all almost below to 1 wt %, they are hidden in the background noise.

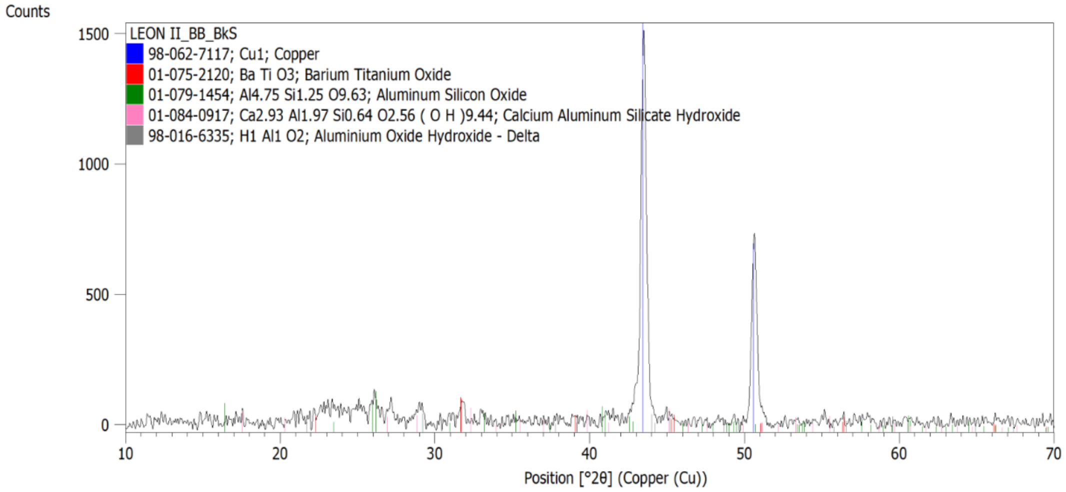


Figure 1: XRD pattern of PCBs' powders from SEAT Leon II.

Table 4 shows the precious elements concentration, in addition to copper and tin, for SEAT Leon III car model.

Table 4: Powders of SEAT LEON III after removal of the above-listed components.

replications, n.	Au, g/t	Ag, g/t	Pd, g/t	Cu, %	Sn, %
1	35.6	497.0	36.7	27.5	0.61
2	11.0	755.6	32.5	28.0	0.58
3	10.9	352.5	31.7	21.4	0.77
average	**19.1**	**535.0**	**33.6**	**25.6**	**0.65**
std dev	14.2	204.2	2.7	3.70	0.10

Concerning with the precious elements a lower concentration of gold was detected with respect Leon II model. Au concentration is 19.1 g/t, Ag 535 g/t and Pd 33.6 g/t. The most present element is copper with a concentration of 25.6 wt %, while Sn is 0.65 wt %.

The sample was also subjected to XRD analysis to identify the form of the previously identified elements and, eventually, other phases. Figure 2 shows the XRD pattern in which the two peaks of copper metal are well identified. Respect to the previous sample also a slight hump to the ranges 18-28 ° is appreciable and indicates the presence of fiberglass. In fact, also a quartz peak was identified around 27°.

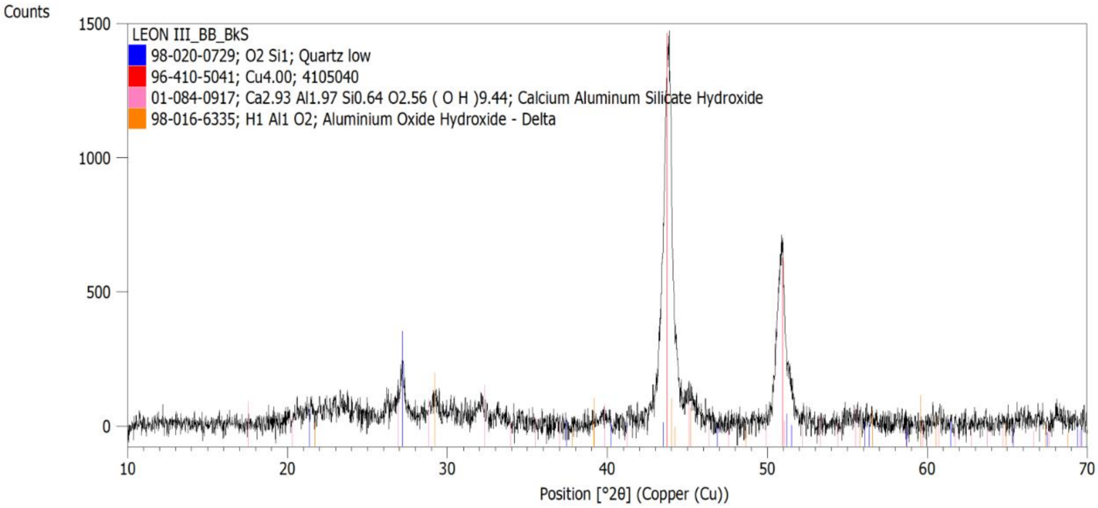


Figure 2: XRD pattern of PCBs' powders from SEAT Leon III.

Table 5 shows the concentration of precious elements (Au, Ag, Pd) and of some base metals like Cu and Sn, for the SEAT model Ibiza IV.

Table 5: Powders of SEAT IBIZA IV after removal of the above-listed components.

replications, n.	Au, g/t	Ag, g/t	Pd, g/t	Cu, %	Sn, %
1	130.8	429.4	31.5	21.0	0.88
2	93.2	325.7	28.9	21.8	1.16
3	63.7	195.3	24.8	16.3	0.74
4	89.2	142.6	24.7	17.4	1.26
average	**94.2**	**273.3**	**27.5**	**19.1**	**1.01**
std dev	27.6	129.4	3.3	2.69	0.24

Concerning with the precious elements the following concentrations are detected: Au 94.2 g/t, Ag 273.3 g/t, Pd 27.5 g/t. The most present element is Cu with a concentration of 19.1 wt %, while Sn is 1.01 wt %.

The sample was also subjected to XRD analysis to identify the form of the previously identified elements and, eventually, other phases. In Figure 3 is shown the XRD pattern, similar results are obtained. Due to the high background noise, only copper peaks are well identified.

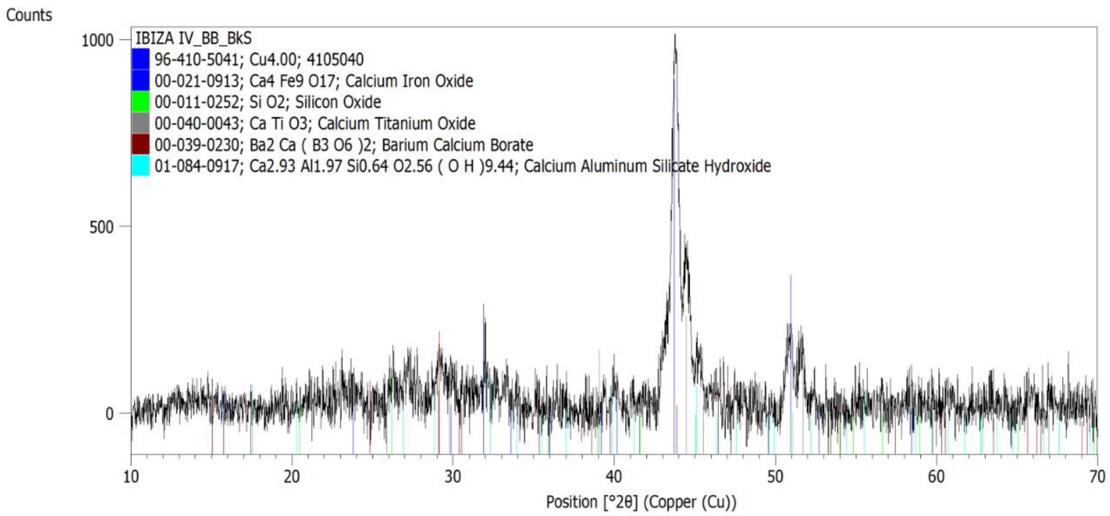


Figure 3: XRD pattern of PCBs' powders from SEAT IBIZA IV.

In addition, also elemental analysis was carried out to determine the C-H-N-S content in the powders. In Table 6, the analysis results are reported for all the car models.

Table 6: CHNS analysis results on the powders of PCBs from different SEAT car models.

car model	run	weight %			
		carbon	hydrogen	nitrogen	sulfur
LEON II	1	21.97	1.79	0.00	0.27
	2	21.04	1.49	0.00	0.29
	average	**21.51**	**1.64**	**0.00**	**0.28**
LEON III	1	19.88	1.79	0.33	0.39
	2	18.29	1.66	0.47	0.26
	average	**19.09**	**1.73**	**0.40**	**0.33**
IBIZA IV	1	22.74	1.71	0.21	0.35
	2	22.50	1.53	0.46	0.24
	average	**22.62**	**1.62**	**0.34**	**0.30**

3.1.2 Components for GDR2 process

Table 7 shows these components for the main board of SEAT 350 LEON II. Chemical characterization of the selected components is shown in Table 8.

Table 7: Different components of the main board of SEAT 350 LEON II with weight percentages to the total weight of electronic board.

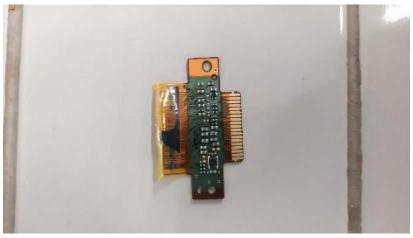
Model	Weight of Board (g)	Name	Photo	Weight [g]	wt %
SEAT 350 LEON II	198.792	Blue connector		7.424	3.73
		Display connector		0.585	0.29
		Small PCB		0.54	0.27

Table 8: Chemical characterization of different components of the main board of SEAT 350 LEON II.

		Blue connector	Display connector	Small PCB
g/ton	Ag	373	434	3161
	Au	12	792	1631
	Pd	25	39	32
	Ti	57	322	69067
	Zn	1260	3092	2771
	Pb	31	118	112
	Cr	10	430	133
	Fe	117	1520	3786
%wt.	Cu	16.54	20.35	24.20
	Ni	1.98	0.72	4.38
	Sn	2.19	2.78	2.98

It is obvious that all selected components have significant amounts of precious metals which means they can be treated by GDR2 process. It should be noted that Pd measurements are associated with some uncertainty, due to its low concentration in the solutions and interferences with other elements during spectrometry. So, it seems there is no Pd in these components.

It should be mentioned that based on visual evaluations it was found that all the above metallic elements in the components (Table 8) presence as alloys, whether in the form of pins or printed metallic path on the boards. Therefore, these elements are dissolved from a metallic phase during leaching.

3.1.3 Components to be removed

This subsection was focused on the characterization of the components that have to be removed in order to avoid that the metal extraction yields are affected by their presence. These components are not suitable to be treated by hydrometallurgical treatments. Concerning with the different car models of SEAT these components are listed in Table 9.

Table 9: Chemical characterization of the components to be removed from SEAT PCBs obtained by ICP-OES analysis. * Metals content from literature studies.

name	photo	weight [g]	wt %	Chemical composition	
Electromagnets		11.43	5.75	metals 53 % plastic 47 %	Cu 26.93 % Fe 15.78 % Zn 0.76 % Nd 0.32 % Mn 0.12 % Sn 0.04 %
Transducer		8.76	4.41	plastic 60 % magnet 34 % other metals 6 %	*Fe 23.2 % *Nd 10.2 % Cu 3.96 % Sn 1.36 % *B 0.32 % *Al 0.10 % Au 12.4 g/t
Aluminum electrolytic capacitor		2.43	1.33	*Al_2O_3 *Pb *rubber	
Crystal oscillator		0.67	0.44	*Cu 62-66 % *Ni 16.5 – 19.5 % *Zn residual %	

Inductors		2.02	1.11	ceramic 74 % metals 26 %	Cu 20.6 % Sn 0.64 % Ag 81 g/t

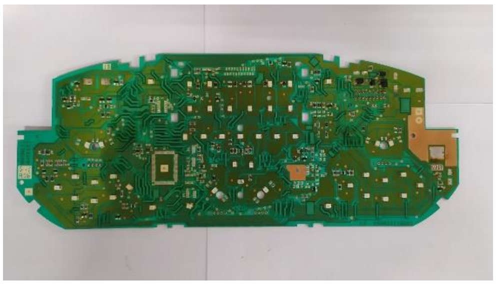
The weight is referred to each component, based on the different car model of SEAT they are present in different units. Concerning with the electromagnets are four in SEAT Leon II, two in SEAT Leon III and SEAT Ibiza IV. Transducer is always one independently by the different models. Aluminum capacitors are not found in SEAT Leon II, while are 5 unit in SEAT Leon III and one in SEAT Ibiza IV. Crystal oscillator instead was found one unit in SEAT Leon II and in SEAT Ibiza IV. Inductors were found only in SEAT Leon III, 3 units.

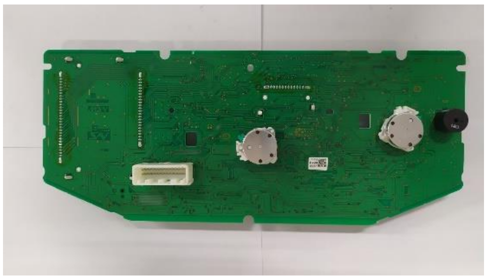
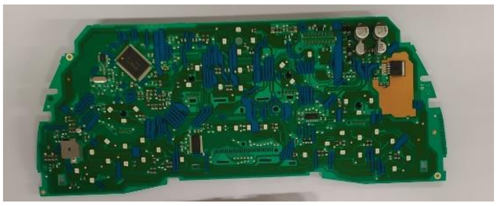
3.2. Car dismantler (POLLINI)

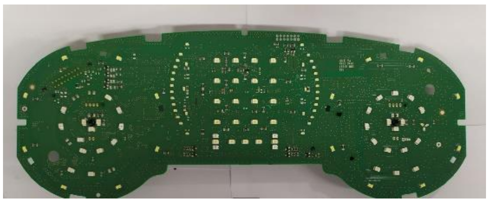
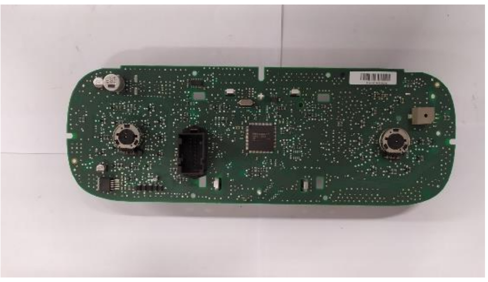
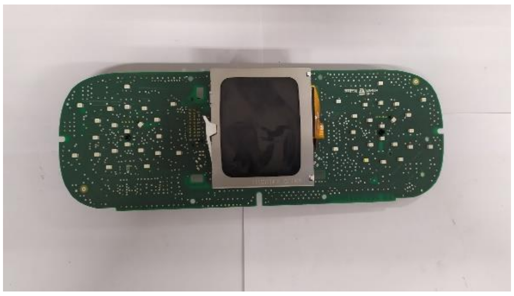
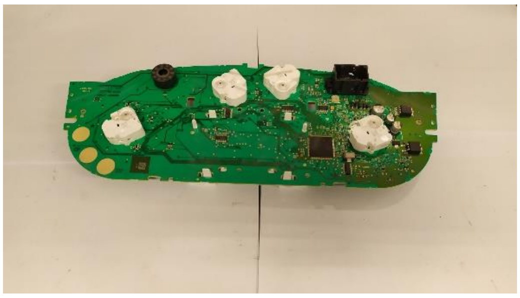
POLLINI has supplied automotive dashboards for 9 different types of cars, mainly from FIAT model, which are shown in Table 10. These dashboards were disassembled and numbered from 1 to 9 according to Table 10.

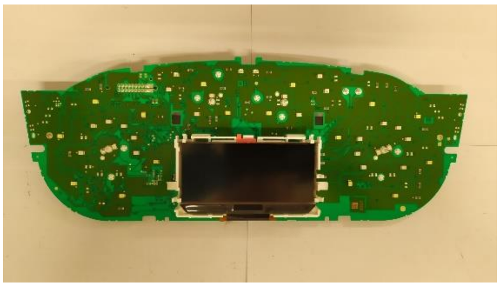
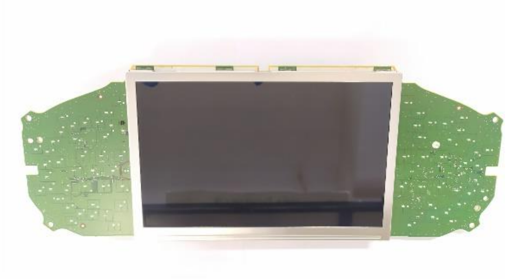
The main electronic boards with different components for each dashboard can be seen in photos in this table.

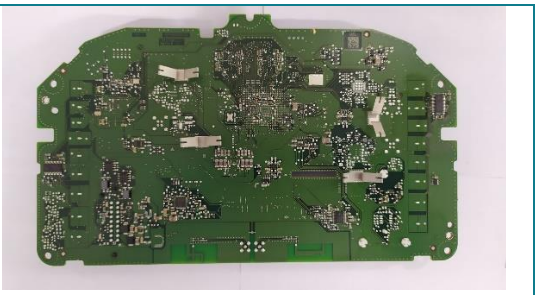
Table 10: Different dashboards provided by POLLINI, numbered based on the written code on their body (can be seen in photo).

Model and Number	Photo	
1		
		

2		
		
3		
		
4		

		
5		
		
6		
		

7		
		
8		
		
9		

As already explained some components are removed to avoid that could inhibit the precious and base metals extraction yields, then the components with a high gold content are also removed to be treated by GDR2 process. Then, the board with some residual components are subjected to grinding operation to obtain a powder with a particle size below to 2 mm to be treated by GDR1 process.

Following sections report the characterization of both the powders and the components with a high gold content.

3.2.1 Powders

In Table 11, the chemical characterization of powders from FIAT BRAVO is reported. The quantitative analysis was performed after chemical attack of the powder and subsequent quantitative analysis by ICP-OES.

Table 11: Powders of PCBs from POLLINI dismantler (Fiat Bravo car model).

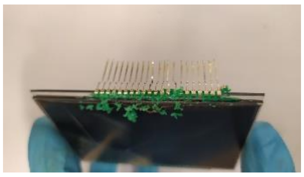
replications, n.	Au, g/t	Ag, g/t	Pd, g/t	Cu, %	Sn, %
1	32.6	348.4	21.1	12.8	1.05
2	15.8	291.8	12.5	12.3	0.55
3	45.4	310.6	18.6	16.0	1.31
4	49.3	628.6	30.1	12.8	0.86
5	37.7	641.5	23.6	12.7	1.08
6	52.8	483.8	30.9	11.7	0.65
average	**38.9**	**450.7**	**22.8**	**13.0**	**0.92**
std dev	12.4	144.1	6.4	1.38	0.26

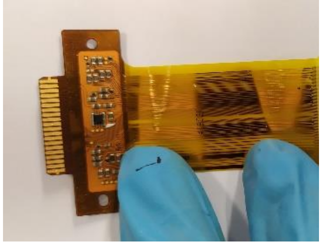
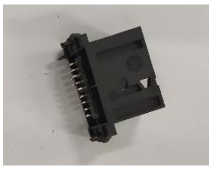
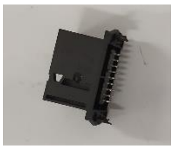
Concerning with the precious elements a lower concentration of gold was detected compared to most SEAT models. Au concentration is 38.9 g/t, Ag 451 g/t and Pd 22.8 g/t. The most present element is copper with a concentration of 13.0 wt %, while Sn is 0.92 wt %.

3.2.2 Components

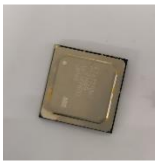
Table 12 shows these components for different dashboards.

Table 12: Different components of each electronic board of dashboards with weight percentages to the total weight of electronic board.

N.	Weight of Board (g)	Name	Photo	Weight [g]	wt %
1	105.1	Black connector		5.616	5.34
		Display connector		0.721	0.69
		Golden wires		0.128	0.12
2	223	White connector		7.254	3.25
		LCD pins		2.23	1
3	166.1	Black connector		5.413	3.26
4	192.6	Black connector		5.553	2.88
		Display connector		0.561	0.29

		Golden wires		0.698	0.36
5	256.6	Black Connector		5.554	2.16
		Display connector		0.702	0.27
		Golden wires		0.332	0.13
6	211.1	Black Connector		5.415	2.56
		Display connector		0.414	0.2
		Golden wires		0.153	0.07
7	235	Black Connector		5.521	2.35
		Display connector		0.89	0.38
		Golden wires		0.259	0.11

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101003587

8	433.2	Black Connector		5.374	1.24
		Display connector		0.464	0.10
		Big Golden wires		3.099	0.71
		CPU		5.415	1.25
9	170.9	Black Connector		5.38	3.15
		Display connector		0.467	0.27
		Big Golden wires		4.766	2.79
		CPU		5.391	3.15

As can be seen from Table 12, different dashboards have some common components that can be removed and treated together. Accordingly, six groups of components selected for characterization, which should be evaluated for leaching experiments with GDR2. The selected groups are Display connectors, small Golden wires, Black connectors, LCD pins, large Golden wires, and CPU. Table 13 shows chemical characterization of these selected groups of components.

Table 13: Chemical characterization of different groups of components of the main boards (POLLINI).

		Display connector	Small Golden wires	Black connectors	LCD pins	large Golden wires	CPU
g/ton	Ag	212	377	232	805	1007	641
	Au	115	752	0	18	375	11
	Pd	40	47	20	158	35	97
	Ti	72	16884	3	1	18070	63
	Zn	3768	1207	68486	1684	5014	1410
	Pb	865	42	853	18	338	13
	Cr	4	46	1	2	22017	20
	Fe	77	534	47	47	104377	337
%wt.	Cu	26.20	36.31	14.04	82.54	37.05	60.67
	Ni	0.82	2.74	0.14	1.01	3.80	1.01
	Sn	2.87	1.07	0.78	11.96	1.85	3.06

It is obvious that all selected groups of components have significant amounts of precious metals which means they can be treated by GDR2 process. As stated before, Pd measurements are associated with some uncertainty, due to its low concentration in the solutions and interferences with other elements during spectrometry. So, it seems there is no Pd in most of these components, except LCD pins. Table 13 shows that LCD pins which were soldered to the electronic board and detached from Display of dashboards No. 2, contain significant amounts of Ag and Pd.

As it can be seen in Table 13, gold content of CPU is very low, but its Ag and Pd content are more significant.

Regarding Ti, Zn, Pb, Cr and Fe, there are huge difference between various groups of components in which, some have low values of these elements, while the others have very high values, which necessitates tracing their path in recovery stage after leaching.

3.3. Identification of the recycling routes

Based on the results of the characterization, two hydrometallurgical recycling routes were defined. A disassembly stage is necessary to obtain the input of the two recycling processes. The sample preparation occurred according to the following steps:

a. Remove specific components that inhibit the recycling rates.
b. Remove specific components to be treated with Gold-REC 2 hydrometallurgical process.
c. Grind the remaining components with the board to be treated with Gold-REC 1 hydrometallurgical process.

In Figure 1, the scheme of the two hydrometallurgical routes for the recovery of base and precious metals from PCBs is shown.

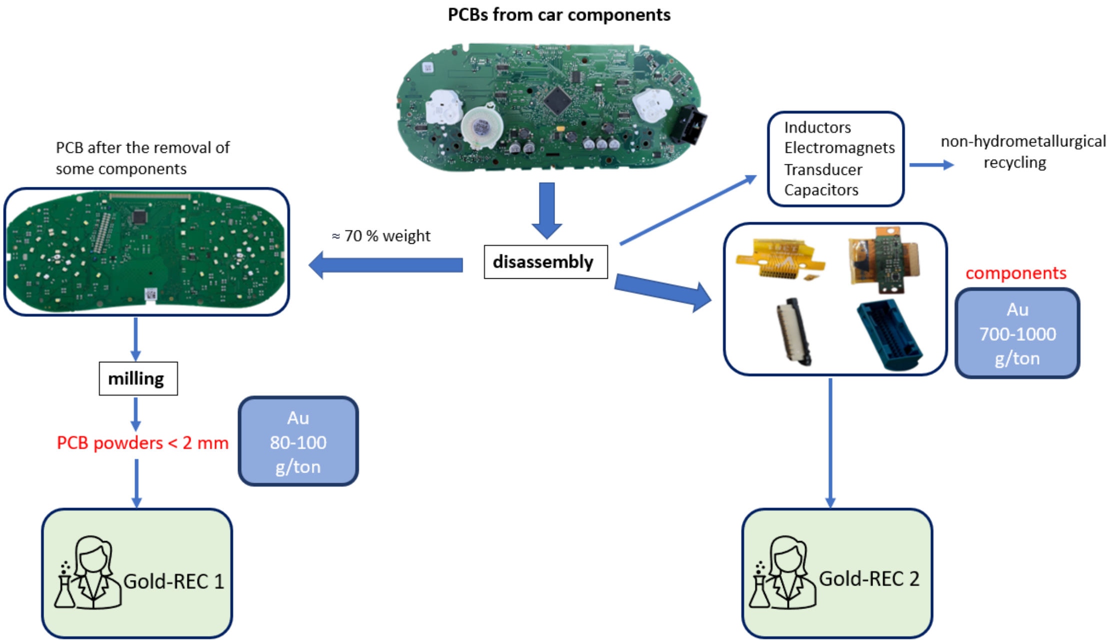


Figure 1: PCBs hydrometallurgical recycling routes.

The PCBs, once manually disassembled from the car component, are subjected to an additional disassembly level. This disassembly is intended to remove some components that inhibit the metal extraction yields during the hydrometallurgical processes, such as components containing organic compounds or with a high copper and aluminum content. These components are for example electromagnets, transducers, inductors, and aluminum capacitors. In addition, with the aim to maximize the recovery yields are also removed some components as connectors, and different components that connect the PCBs with the LCDs like the flexible board and the small PCBs. These last components are removed for their high gold content (700 – 1000 g/t) and because can be processed by Gold-REC 2 without any size reduction (International Publication number: WO2019/229632). The remaining part of PCB, from which several components have been removed but remain the integrated circuit chips and other valuable components, is subjected to a grinding process to obtain a dimensional reduction until a powder with a particle size less than 2 mm. The obtained powder, with a gold content in the range of 80 – 100 g/t, can be treated by Gold-REC 1 hydrometallurgical process to recover base and precious metals (International Publication number: WO2018/215967).

In the present document Gold-REC 1 and Gold-REC 2 hydrometallurgical processes are studied on different combi-instrument PCBs to optimize their operative conditions with the aim to maximize the recycling yields and to reduce the chemical consumption and the production of wastewaters.

4. Recycling process optimization – powders (GDR1)

This section includes the hydrometallurgical tests aimed at the treatment of the PCBs powders with a 2 mm particle size, obtained after disassembly and grinding operations. The hydrometallurgical process to essentially recover base metals such as copper and tin, and precious metals as gold, silver and palladium was studied starting by GDR1 UNIVAQ patent. Tests were planned to optimize the process to maximize the extraction yields and to reduce the chemical consumption, and the production of wastewater according a MLD approach. Leaching stages were the chemical operations that concerned process optimization studies. Since the intrinsic economic value of PCB powders mainly depend on gold, the focus of the process optimization studies was on gold recovery.

4.1. Leaching tests

4.1.1 Addition of a leaching stage to GDR1 process

Firstly, PCBs powders from different SEAT car models (Leon II, Leon III, and Ibiza IV) were subjected to GDR1 process also with the addition of one more step to dissolve base metals. Operative conditions for the base metals leaching were solid concentration 15 % w/v, sulfuric acid 1.8 mol/L, H_2O_2 (30 % w/v) 20 % v/v, room temperature, stirring 200 rpm, and time of reaction 1.5 h. The dissolution of precious metals instead occurred at the following operative conditions: solid concentration 10 % w/v, thiourea 20 g/L, Fe^{3+} 6 g/L, sulfuric acid 0.2 mol/L, room temperature, stirring 300 rpm, time of reaction 1 h.

In Table 14, the obtained results for powder from Leon II, according to each step of leaching were reported. More in detail, the concentration of precious metals (Au, Ag, Pd) and base metals (Cu, Sn) in the leach liquor solutions are shown, such as the recovery yields for each output.

Table 14: Gold-REC 1 test on the powders of SEAT LEON II.

Leaching step	Au, mg/L	Ag, mg/L	Pd, mg/L	Cu, mg/L	Sn, mg/L
1 – base metals (1st)	0.1	27.9	1.8	17245	439.2
2 – base metals (2nd)	0.0	0.2	0.1	1187	102.0
3 – precious metals	4.3	85.4	0.3	92.3	20.3
recovery yields, %					
1 – base metals (1st)	0.6	18.5	59.8	84.2	58.4
2 – base metals (2nd)	0.0	0.1	4.5	5.8	19.6
3 – precious metals	54.5	70.6	10.8	0.6	4.2
remained in the solid residue	44.9	10.8	24.1	9.4	17.8
	Au, %	**Ag, %**	**Pd, %**	**Cu, %**	**Sn, %**
recovery in the correct step	54.5	70.6	24.1	90.0	82.2
summary					
Solid	wt %		Au, g/t		
Feed	100.0		81.5		
Solid residue	82.0		28.0		

The results show that 54.5 % of gold dissolution was achieved. A higher value was not obtained probably because, compared to the GDR1 patent, this material has a lower initial concentration of gold. There is always a certain amount of gold in the solid residue that is not recovered by the process. As regards silver recovery, it was observed a partial dissolution also in the first base metals leaching; therefore, the recovery of silver in the correct step was 70.6 %. This result could depend on that silver does not need a complexing agent to be dissolved with respect to gold. Palladium initial concentration, slightly more than 20 g/t, it too low to assume a recovery. If the initial content of palladium was higher, the remaining palladium in the final solid residue of the process could be recovered by a subsequent leaching system. In this case, also due to partial dissolutions, the final content of palladium in the solid residue is too low to assume its recovery. Copper dissolution was 90 % and tin 82.2 %.

To increase the gold dissolution yields, a new test was performed at the same conditions but adding one more base metal leaching stage. In Table 15, the results are reported.

Table 15: Gold-REC 1 with the addition of an extra step on the powders of SEAT LEON II.

Leaching step	Au, mg/L	Ag, mg/L	Pd, mg/L	Cu, mg/L	Sn, mg/L
1 – base metals (1st)	0.0	36.0	0.2	19536	488.0
2 – base metals (2nd)	0.0	8.1	0.1	2456	190.6
3 – base metals (3rd)	0.0	3.5	0.0	685	91.0
3 – precious metals	5.0	64.2	< 0.1	22.6	3.1
recovery yields, %					
1 – base metals (1st)	0.0	24.3	45.1	84.0	61.4
2 – base metals (2nd)	0.0	5.5	27.5	10.6	24.0
3 – base metals (3rd)	0.0	2.3	0.0	0.0	0.0
3 – precious metals	57.8	53.2	8.6	0.1	0.5
remained in the solid residue	42.2	14,7	18.8	5.3	14.2
	Au, %	**Ag, %**	**Pd, %**	**Cu, %**	**Sn, %**
recovery in the correct step	57.8	53.2	18.8	94.6	85.3
summary					
Solid	wt %		Au, g/t		
Feed	100.0		81.5		
Solid residue	80.1		27.8		

Gold dissolution yields was 57.8 %, only just higher than the previous test. The residual gold content not recovered is 27.8 g/t, really like to what was obtained in Table 14. The additional leaching stage of base metals had the effect of increasing the copper dissolution yield up to almost 95 %, and slightly reducing the solid residue weight. So, the addition of the additional step is almost negligible on gold recovery and not justifiable.

The same test pair, adopting the GDR1 process and the process with an addition step of base metals leaching, were performed for the powders from SEAT Leon III model, even if the initial gold concentration, 19.1 g/t, is much lower than the other models. In Table 16 the results of the GDR1 process are reported.

Table 16: Gold-REC 1 test on the powders of SEAT LEON III.

Leaching step	Au, mg/L	Ag, mg/L	Pd, mg/L	Cu, mg/L	Sn, mg/L
1 – base metals (1st)	< 0.1	13.5	3.5	30614	656.4
2 – base metals (2nd)	0.0	1.4	0.5	3781	271.1
3 – precious metals	1.9	57.2	0.2	74.2	6.0
recovery yields, %					
1 – base metals (1st)	1.3	14.3	75.1	85.3	52.6
2 – base metals (2nd)	0.0	1.5	9.8	10.5	21.7
3 – precious metals	71.2	66.6	5.3	0.0	0.5
remained in the solid residue	27.5	13.6	9.8	0.2	25.2
	Au, %	**Ag, %**	**Pd, %**	**Cu, %**	**Sn, %**
recovery in the correct step	71.2	66.6	9.8	95.8	74.3
summary					
Solid	wt %		Au, g/t		
Feed	100.0		19.1		
Solid residue	71.8		5.8		

The results show as 71.2 % of gold extraction was achieved by adopting the GDR1 process. Concerning with the dissolution yields of the other metals: Ag 66.6 %, Cu 95.8 %, and Sn 74.3 %. Also in this case, palladium is too low in the initial sample to recover it.

In Table 17, the results of the test carried out with an additional extra step of base metals leaching are shown.

Table 17: Gold-REC 1 with the addition of an extra step on the powders of SEAT LEON III.

Leaching step	Au, mg/L	Ag, mg/L	Pd, mg/L	Cu, mg/L	Sn, mg/L
1 – base metals (1st)	< 0.1	13.5	0.3	32787	656.4
2 – base metals (2nd)	0.0	1.4	< 0.1	2694	271.1
3 – base metals (3rd)	0.0	0.0	< 0.1	1106	74.6
3 – precious metals	1.7	57.2	< 0.1	17.2	6.0
recovery yields, %					
1 – base metals (1st)	1.1	14.2	70.3	86.5	49.3
2 – base metals (2nd)	0.0	1.5	9.1	7.1	20.4
3 – base metals (3rd)	0.0	0.0	2.3	2.9	5.6
3 – precious metals	66.1	66.4	7.0	0.0	0.5
remained in the solid residue	32.8	17.9	11.3	3.5	24.2
	Au, %	**Ag, %**	**Pd, %**	**Cu, %**	**Sn, %**
recovery in the correct step	66.1	66.4	11.3	96.6	75.3
summary					
Solid	wt %		Au, g/t		
Feed	100.0		19.8		
Solid residue	71.1		6.0		

Gold extraction as shown in the previous table is 66.1 %, slightly less than obtained in GDR1 test. Therefore, for the treatment of this materials, seems that the additional step of base metals leaching does not allow to increase gold rate dissolution. The other recovery yields are the following: Cu 96.6 %, Sn 75.3 %, Ag 66.4 %.

Then, for the treatment of SEAT Ibiza IV powders of PCBs was carried out a GDR1 test, performed at the patent operative conditions also listed at the beginning of this subsection. In Table 18 the obtained results are reported.

Table 18: Gold-REC 1 test on the powders of SEAT IBIZA IV.

Leaching step	Au, mg/L	Ag, mg/L	Pd, mg/L	Cu, mg/L	Sn, mg/L
1 – base metals (1st)	0.1	73.6	3.0	26613	1702
2 – base metals (2nd)	0.0	0.7	0.2	1509	133.3
3 – precious metals	5.5	32.6	0.2	40.6	12.9
recovery yields, %					
1 – base metals (1st)	0.1	56.2	71.8	92.9	75.5
2 – base metals (2nd)	0.0	0.6	4.1	5.3	5.9
3 – precious metals	59.3	28.7	3.9	0.2	0.7
remained in the solid residue	40.6	14.5	9.8	1.6	17.9
	Au, %	**Ag, %**	**Pd, %**	**Cu, %**	**Sn, %**
recovery in the correct step	59.3	28.7	9.8	98.2	81.4
summary					
Solid	wt %		Au, g/t		
Feed	100.0		94.2		
Solid residue	73.8		27.7		

Based on the experimental results, by adopting GDR1 process, a gold dissolution of 59.3 % was achieved. The residual gold content in the solid after all the leaching stages is 27.7 g/t, without considering the weight loss. Then, silver recovery is 28.7 %, this low value depends on the silver dissolution that also occurred in the first base metal leaching. Probably, strongly oxidant conditions in the first step determine the silver dissolution. Regarding the other metals, 98.2 % of copper dissolution and 81.4 % of tin occurred.

In order to maximize gold extraction, but also to avoid the silver dissolution in the first step, a factorial experimentation was planned.

4.1.2 *Factorial experimentation*

After evaluated the results obtained by the adoption of GDR1 process, a factorial experimentation to evaluate the effect of some factors was planned. These tests were performed on the treatment of PCBs powders from SEAT Ibiza IV model. Based on the results reported in Table 18, to avoid the silver dissolution in the first step of base metals leaching but also with the aim to reduce the chemical consumption, concentration of H_2O_2 in the first and in the second leaching steps was studied. More in detail, H_2O_2 (30 % w/v) was studied in the range 10 – 20 % v/v for both stages. Therefore, with respect to the GDR1 patent in which the H2O2 was 20 % v/v, these tests aim to evaluate if a lower concentration can be adopted. In addition, also the effect of the third leaching step was studied in a systematic way since from the results in the section 4.1.1 seemed negligible.

In Table 19, the selected factors and their respective levels in carrying out the factorial experimentation were reported.

Table 19: Factors and levels for the factorial experimentation on powders of SEAT Ibiza IV.

Factor		unit	Level	
			-1	1
A – quantitative	H_2O_2 concentration in the 1st step	% v/v	10	20
B – quantitative	H_2O_2 concentration in the 2nd step	% v/v	10	20
C – categoric	Presence of the 3rd leaching step	-	NO	YES

Factor C is a qualitative/categoric factor since the aim was to evaluate the effect when it was carried out or not. In Table 20, all the performed tests in order to evaluate the effect of the selected factors in the gold dissolution yields were shown, with the conditions for each factor. The other operative conditions, not reported in the table, were those of GDR1 process. Last two columns report the response of each test that are related to the gold recovery.

Table 20: Factors and levels for the factorial experimentation on powders of SEAT Ibiza IV.

Test no.	Combination	Factor			Au		
		A	B	C	dissolution %	concentration mg/L	solid residue content g/t
1	(-1)	10	10	NO	54.3	5.35	35.4
2	a	20	10	NO	62.5	4.57	24.5
3	b	10	20	NO	48.9	4.67	42.8
4	ab	20	20	NO	55.5	4.36	29.3
5	**c**	**10**	**10**	**YES**	**69.8**	**4.42**	**16.4**
6	ac	20	10	YES	61.4	5.11	24.8
7	bc	10	20	YES	67.7	5.11	18.1
8	abc	20	20	YES	68.8	6.20	21.8
9	I	15	15	YES	65.6	4.25	19.5
10	II	15	15	NO	52.0	4.70	38.6

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Run test 5 allowed to achieve a higher gold dissolution yield, almost 70 %; it was carried out at low level for factor A and B, and with the presence of factor C. Therefore, the operative conditions were 10 % v/v of hydrogen peroxide for the first two base metals leaching, that are the conditions that allow to save chemical; but it seems necessary the third step to maximize the gold extraction. Last column showed the gold content not recovered for each test; we can see how the lowest value 16.4 g/t was obtained for run 5. The analysis of the variance (ANOVA) by Yates algorithms has allowed to process the data with the aim of evaluating the level of significance to 95 % of the three factors and their interactions, within the investigated ranges.

Table 21: ANOVA of the factorial experimentation.

Source	Coefficient	Sum of Squares	F-value	p-value	Level of significance 95 %
A-H_2O_2 concentration first step	0.94	7.03	0.829	0.459	54.13
B-H_2O_2 concentration second step	-0.89	6.30	0.743	0.480	52.05
C- third step	6.01	361.20	42.59	0.023	**97.73**
AB	0.99	7.80	0.920	0.439	56.13
AC	-2.76	61.05	7.20	0.115	88.84
BC	2.21	39.16	4.62	0.165	83.53
A^2	2.31	8.56	1.01	0.421	57.91

The only significant factor is factor C, relative to the presence of the third leaching step of the base metals. The level of significance is 97.73 %. For all other factors and interactions values of less than 95 % have been obtained indicating no significance. The coefficient sign must be evaluated to know whether the significance has a positive or negative effect on the gold extraction yield. In the case of factor C, the presence of the third step positively affects the extraction of gold. For the other factors, since there is no significance on the gold response, it is possible to work at the conditions to reduce reagent consumption and therefore process operating costs.

4.1.3 *Optimized recycling process*

Based on the factorial experimentation results, the operative conditions to maximize the gold extraction were defined. Operative conditions are listed below:

- First base metals leaching step (H_2O_2 10 % v/v, H_2SO_4 1.8 mol/L)
- Second base metals leaching step (H_2O_2 10 % v/v, H_2SO_4 1.8 mol/L)
- Third base metals leaching step (H_2O_2 15 % v/v, H_2SO_4 1.8 mol/L)
- Precious metals leaching step (thiourea 20 g/L, Fe^{3+} 6 g/L, H_2SO_4 0.2 mol/L)

The reduction of hydrogen peroxide to 10 % also for the third step could be investigated. Table 22 shows the full detailed results of test 5.

Table 22: Test 5 of factorial experimentation.

Leaching step	Au, mg/L	Ag, mg/L	Cu, mg/L	Sn, mg/L
1 – base metals (1st)	< 0.1	2.7	20236	1800
2 – base metals (2nd)	0.0	0.0	5012	54.7
3 – base metals (3rd)	0.0	0.0	2478	7.8
3 – precious metals	4.4	163.2	118	5.9
recovery yields, %				
1 – base metals (1st)	0.0	1.2	69.5	92.7
2 – base metals (2nd)	0.0	0.0	17.2	2.8
3 – base metals (3rd)	0.0	0.0	8.5	0.4
3 – precious metals	69.8	88.8	0.5	0.4
remained in the solid residue	30.2	10.0	4.7	3.6
	Au, %	**Ag, %**	**Cu, %**	**Sn, %**
recovery in the correct step	69.8	88.8	95.3	96.0
summary				
Solid	wt %		Au, g/t	
Feed	100.0		94.2	
Solid residue	78.3		16.4	

By this test the following dissolution yields are obtained: Au 69.8 %, Ag 88.8 %, Cu 95.3 %, Sn 96.0 %. So, in addition to an increase in gold recovery, working at a lower concentration of hydrogen peroxide in the first two steps reduces the dissolution of silver and then is recovered mainly in the correct step of precious metals leaching.

The reason why it is not possible to guarantee recovery of more than 70 % of gold could be dependent on the initial content, in fact, in the process of solid output, there is always a certain content of gold not recovered between 10 and 20 g/t. If there had been a higher concentration of gold in the initial powders, the recovery would have been higher.

Then, in order to reduce chemical consumption according to an MLD approach, three multistage base metals leaching was studied by a counter-current scheme. Figure 2 shows the counter-current configuration.

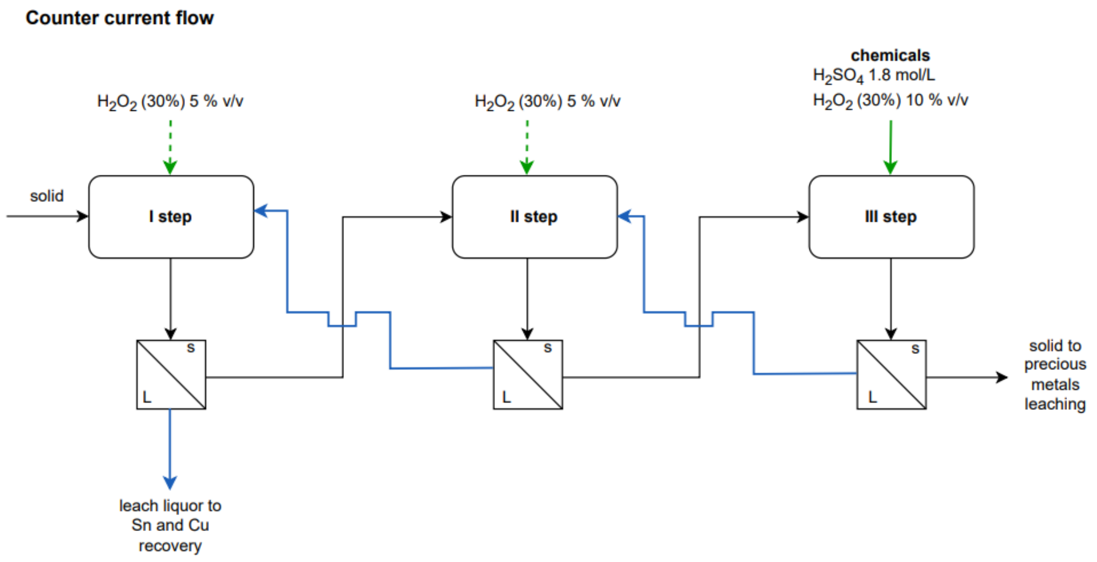


Figure 2: Counter current multistage base metals leaching scheme.

The above shown counter-current configuration was studied for two cycles and similar extraction yields to those obtained in Table 22 are achieved. In Figure 3 is shown a scheme for the recovery of Sn, Cu and precious metals from the solutions in which they were dissolved. The counter-current scheme shown in Figure 2 concerns the base metals leaching, instead, in Figure 3 is reported as 1st leaching stage.

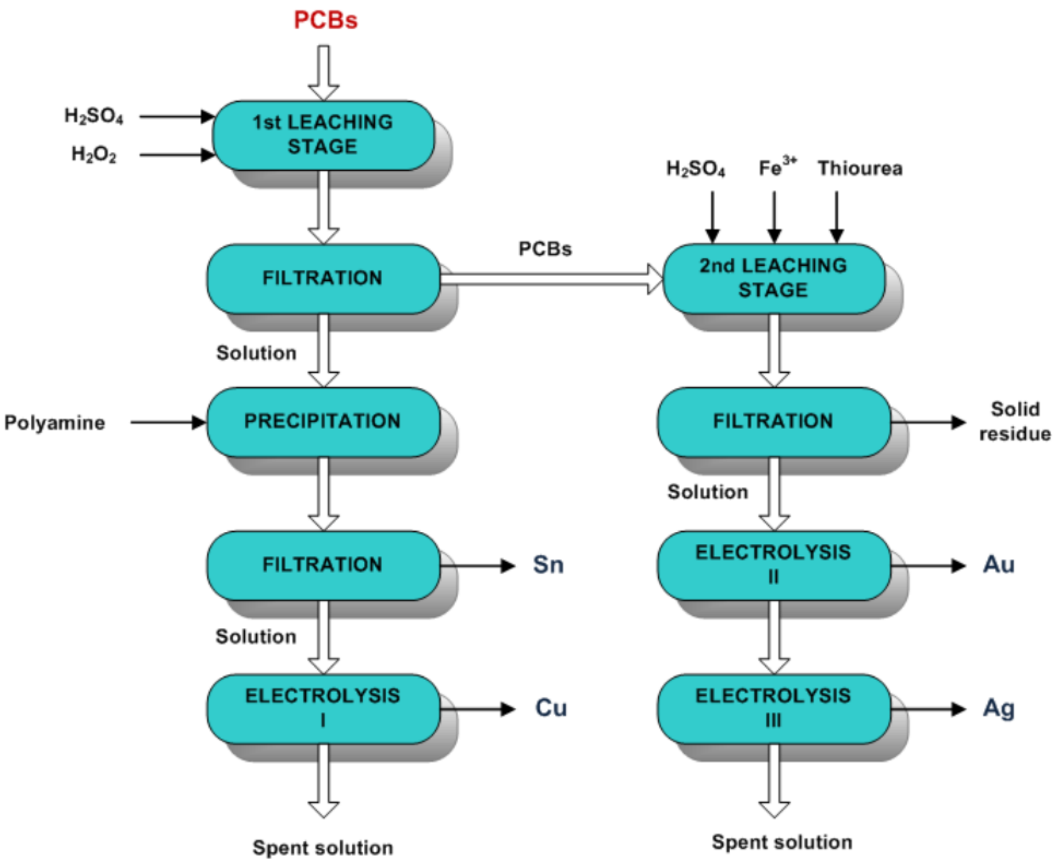


Figure 3: Gold-REC 1 recycling process flowsheet.

Therefore, in the first stage, base metals such as copper (Cu) and tin (Sn) are extracted, whereas precious metals, i.e., gold (Au) and silver (Ag), are brought into solution in the second stage.

4.2. Recovery of base and precious metals from the solution

4.2.1. Tin recovery

The pregnant solution from the first leaching stage undergoes tin precipitation by adding a cationic flocculant, polyamine, with a concentration of 2.5 mL/L of solution. The polyamine must be diluted with distilled water to a concentration of 10% w/v. The solution is slowly mixed at 50–100 rpm at room temperature for 30 min, a sufficient time to precipitate the metastannic acid according to the following reaction:

$$polyamine + 2\,SnSO_4 + \ 2\,H_2SO_4 \rightarrow \ 2\,H_2SnO_3 + 3\,SO_4{}^{2-}$$

The precipitation yield is nearly 90%. In Table 23 are reported the obtained results.

Table 23: Results for the recovery of Sn from the leach liquor solutions

Tin recovery	Sn before the treatment, mg/L	Sn after the treatment, mg/L	Sn recovery, %
Solution from the first cycle	1767.8	282.48	84.0
Solution from the second cycle	2415.7	145.9	93.8

Both tests show good efficiency of the process, which allowed the average recovery of about 90 % of tin. The tin content in the precipitate obtained is around 50 % because metastannic acid has several water molecules. The metastannic acid was oxidized at 650 °C for 1 h to obtain, as the final product, tin oxide with a grade of 97.4 % with copper at 1.8 % and polyamine as the main impurities.

4.2.2. Copper recovery

The solution resulting from filtration and containing copper sulphate undergoes electrowinning. The cathode is made of copper, whereas the anode is made up of graphite. The current density is 250 A/m^2, voltage 2.0 V, and the deposition time 1 h, room temperature. While copper is recovered at the cathode by reducing Cu^{2+} ions, water is oxidized at the anode, generating H_3O^+ ions. Thus, the spent solution is almost acid, most of which can be recycled back to the first leaching stage. This allows the recovery of the remaining copper that cannot be discharged completely not to lower the current efficiency. In order to determine the optimum working voltage on the basis of the solution to be treated, a test was carried out to determine the discharge potential (Figure 4).

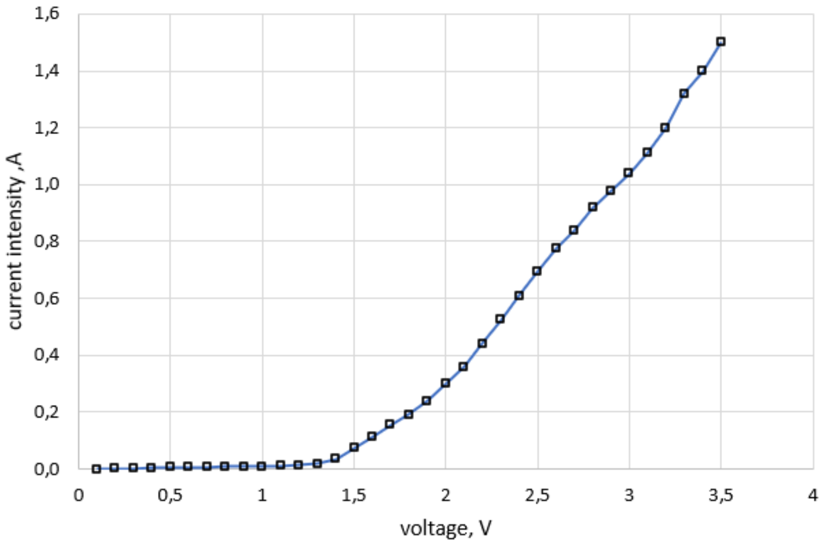


Figure 4: Determination of discharge potential for copper electrowinning

The voltage curve as a function of current was obtained by gradually increasing the voltage from 0.1 V to 3.5 V and the corresponding current values were measured. The obtained curve showed an increase in slope from 1.3 V. Therefore, an immediately higher voltage (1.5 V) was selected for the conduction of the copper electrodeposition tests. Since preliminary test was not allowed to recover copper at this condition, the voltage was increased to 2 V.

In Figure 5, pictures at the beginning and at the end of copper electrowinning are shown.

Figure 5: Copper recovery from electrowinning (at the beginning and at the end of the test)

It can be observed that the solution becomes almost transparent after 2 hours of electrowinning treatment. Copper material was used for the cathode and graphite for the anode. The high copper content in the solution means that, as the electrodeposition continues, there is no longer available surface on the cathode for the recovery of copper. For this reason, part of the copper powder is on the bottom of the flask. Copper recovery from the solution as a function of current efficiency at different times is shown in the following figure (Figure 6). The blue curve is for copper recovery, and the orange one is for the current efficiency.

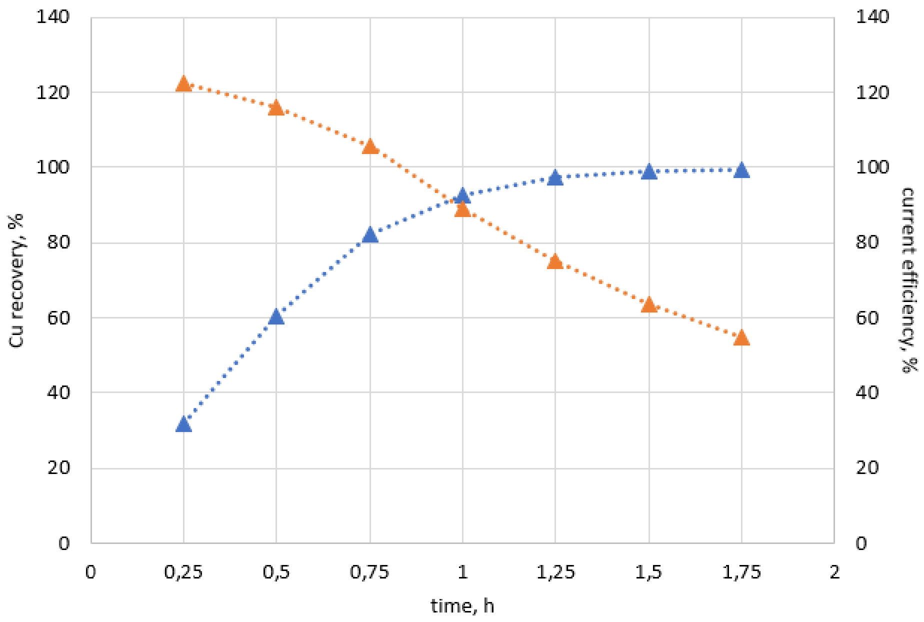


Figure 6: Copper recovery vs current efficiency for the electrowinning test

The intersection of the two curves indicates the condition for avoiding excessive energy consumption. After 1 h of electrodeposition a recovery of 97 % of copper was obtained. The calculated energetic consumption is 2.1 kWh/kg.
Below are the chemical reactions that occurred to the cathode and anode:

$$Cu^{2+} + 2\,e^- \rightarrow Cu^0$$

$$H_2O \rightarrow H^+ + OH^- \rightarrow 0.5\,O_2 + 2H^+ + 2\,e^-$$

As regards the purity of copper, determined after a chemical attack, around 99 % was obtained; impurities consist of aluminum, iron, zinc, and traces of nickel.

4.2.3. Gold-silver recovery

Gold and silver are theoretically recovered by two sequential electrowinning stages, with the following operating conditions:

a. Gold:
   - anode: graphite;
   - cathode: graphite;
   - current density: 50 A/m^2;
   - cell voltage: 1.2 V;
   - time: 2 h;
   - temperature: 25 °C.

b. Silver:
   - anode: graphite;
   - cathode: copper;
   - current density: 75 A/m^2;
   - cell voltage: 1.5 V;
   - time: 2 h;

- temperature: 25 ◦C.

Below is reported the chemical reaction that occurs to the cathode:

$$(Au(CS(NH_2)_2)_2)^+ + e^- \rightleftarrows Au^{0} + 2\,CS(NH_2)_2$$

Preliminary gold electrodeposition tests showed that a selective recovery of gold and silver could not be achieved. In fact, silver was deposed simultaneously by working at 1.2 V in addition to gold. By decreasing the voltage even slightly, no gold recovery was observed. In Figure 7, the recovery of gold and silver as a function of their current efficiencies are showed during the electrodeposition.

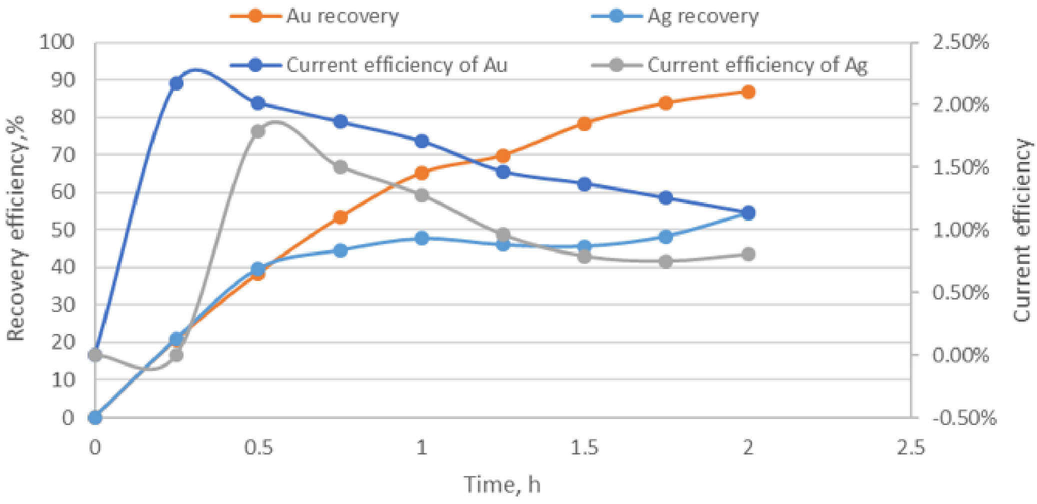


Figure 7: Gold-silver recovery vs current efficiency for the electrowinning test

Approximately 85% of gold and 55% of silver were recovered after two hours of treatment with low current efficiencies. Current efficiencies are low due to low concentrations of gold and silver in the solution and the presence of parasitic reactions. The current consumption is about 10 kWh/kg of Au. Due to the very low quantities of the solid deposited by the equipment used in the laboratory scale, an accurate determination of the purity of the product obtained is not possible at this stage. Based on the obtained recoveries, gold-silver alloy (dorè) has about 29 % of gold grade and 71 % of silver grade. Therefore, further treatment by using a leaching system without a complexing agent could allow the separating of gold from silver.

5. Recycling process optimization – components (GDR2)

5.1. Preliminary leaching tests

In this section GDR2 process is employed for the recovery of precious metals from different components of the main board of SEAT 350 LEON II (Table 7), and six selected groups of components of 9 dashboards of POLLINI (Table 12), which were defined previously. Two steps of leaching were performed according to the conditions stated in GDR2, to have high leaching efficiency for all elements. Leaching experiments were performed in a solution containing 30% HCl (37%), 20% H_2O_2 (30%) and 10% $C_2H_4O_2$ (99%) with a pulp density of 15-20% for most of the experiments, for 5 hours at room temperature without stirring. 100% for hydrogen peroxide and 50% for HCl was made up before second leaching for all solutions. Metal recovery in each stage of leaching is presented in Table 24 and Table 25 for the components of SEAT 350 LEON II, and six selected groups of components of 9 dashboards of POLLINI, respectively.

A selective gold recovery stage should be performed on the leaching solution before going to the second stage of leaching, with a reduction with ascorbic acid (5 g/L). In this stage 5 g/l of citric acid is added firstly, to react with the remained H_2O_2 in the solution. Then ascorbic acid is added to reduce Au into metallic state in the form of precipitates, which is separated by filtration.

It should be noted, for golden wire groups of components in the dashboards provided by POLLINI, a thermal treatment at 600 °C for 2 hours was performed before second leaching, to remove the protective layer on the wires and exposing the metal surface of wires to the solution.

Table 24: Metal recovery in each stage of leaching for different components of the main board of SEAT 350 LEON II.

Groups of components	Elements	Extraction yield (%)		Remained value in solid residue	Total
		1st stage of leaching	2nd stage of leaching		
Blue connector	Ag	88.12	7.55	4.33	100
	Au	72.49	3.64	23.87	100
	Pd	83.97	9.17	6.86	100
	Ti	4.29	22.02	73.69	100
	Zn	76.96	12.17	10.87	100
	Pb	32.82	62.84	4.34	100
	Cr	0	71.67	28.33	100
	Fe	7.98	12.63	79.39	100
	Cu	77.70	11.51	10.79	100
	Ni	89.91	7.92	2.17	100
	Sn	87.76	5.89	6.35	100
Display connector	Ag	71.06	19.88	9.06	100
	Au	8.82	39.97	51.21	100
	Pd	61.96	38.04	0	100
	Ti	0	64.62	35.38	100
	Zn	36.57	15.99	47.44	100
	Pb	7.55	92.45	0	100
	Cr	0.42	98.59	0.99	100
	Fe	3.22	88.76	8.02	100
	Cu	72.92	25.78	1.30	100
	Ni	99.42	0	0.58	100
	Sn	75.68	15.47	8.85	100
Small PCB	Ag	24.87	3.16	71.97	100
	Au	28.64	5.04	66.32	100
	Pd	11.29	1.40	87.31	100
	Ti	18.69	29.85	51.46	100
	Zn	11	3.57	85.43	100
	Pb	43.89	4.03	52.08	100
	Cr	1.82	90.51	7.67	100
	Fe	10.10	4.85	85.05	100
	Cu	12.92	4.97	82.11	100
	Ni	32.50	20.49	47.01	100
	Sn	93.07	2.89	4.04	100

Table 24 shows that two step of leaching is sufficient to recover more than 75% of precious metals in the blue connector component, while the recovery of precious metals in display connector and small PCB is not satisfactory and most of gold, in display connector, and most of all precious metals in small PCB remained in the final solid residue. The reson for low leaching efficiency is probably the presence of high value of other elements such as Ni, Ti and Cu in these components which use reagents and reduces reagent's concentration in the solution. High content of these elements can also interfere the dissolution of gold. In addition, improper immersion of small PCB in the solution can also be considered as a reason for low recovery of precious metals during leaching.

Table 25: Metal recovery in each stage of leaching for six selected groups of components (POLLINI).

Groups of components	Elements	Extraction yield (%)		Remained value in solid residue	Total
		1st stage of leaching	2nd stage of leaching		
Display connectors	Ag	93.67	0	6.33	100
	Au	27.43	19.20	53.37	100
	Pd	53.15	28.54	18.30	100
	Ti	3.67	0	96.33	100
	Zn	46.68	26.22	27.10	100
	Pb	99.32	0	0.68	100
	Cr	4.82	0	95.18	100
	Fe	12.57	0	87.43	100
	Cu	52.13	28.89	18.98	100
	Ni	98.85	0	1.15	100
	Sn	65.37	17.56	17.06	100
small Golden wires	Ag	41.87	45.15	12.98	100
	Au	83.18	10	6.82	100
	Pd	9	91	0	100
	Ti	40.60	0	59.40	100
	Zn	30.71	50.81	18.48	100
	Pb	85.43	0	14.57	100
	Cr	78.47	0	21.53	100
	Fe	64.43	0.81	34.76	100
	Cu	18.76	81.08	0.16	100
	Ni	65.97	0	34.03	100
	Sn	96.5	0	3.5	100
Black connectors	Ag	95	1.36	3.64	100
	Au	0	0	0	0
	Pd	80.37	4.08	15.55	100
	Ti	10.89	0	89.11	100
	Zn	63.59	23.31	13.10	100
	Pb	87.85	8.54	3.61	100
	Cr	77.5	0	22.5	100
	Fe	67.05	9.33	23.62	100
	Cu	73.59	11.84	14.57	100
	Ni	87.37	6.70	5.93	100
	Sn	98.08	0.95	0.97	100

LCD pins	Ag	91.46	0	8.54	100
	Au	55.27	21.74	22.99	100
	Pd	56.74	23.63	19.63	100
	Ti	0	0	0	0
	Zn	17.53	63.91	18.56	100
	Pb	52.33	20.60	27.07	100
	Cr	62.47	0	37.53	100
	Fe	42.26	0	57.74	100
	Cu	31.79	43.78	24.43	100
	Ni	79.13	19.98	0.89	100
	Sn	79.38	6.98	13.64	100
large Golden wires	Ag	11.71	22.86	65.43	100
	Au	1.66	1.92	96.42	100
	Pd	17.36	68.04	14.60	100
	Ti	1.08	0	98.92	100
	Zn	41.33	29.50	29.17	100
	Pb	3.75	87.93	8.32	100
	Cr	30.60	45.15	24.25	100
	Fe	28.35	45.73	25.92	100
	Cu	12.38	69.64	17.98	100
	Ni	32.50	9.37	58.13	100
	Sn	83.13	7.38	9.49	100
CPU	Ag	35.24	26.37	38.39	100
	Au	57.95	14.99	27.06	100
	Pd	12.40	19.35	68.25	100
	Ti	0	0	100	100
	Zn	6.30	11.32	82.38	100
	Pb	55.88	0	44.12	100
	Cr	10.68	84.74	4.58	100
	Fe	7.80	52.50	39.70	100
	Cu	7.65	24.53	67.82	100
	Ni	63.70	9.70	26.60	100
	Sn	99.51	0	0.49	100

Table 25 shows that two stages of leaching are efficient in achieving extraction yields more than 75% for all elements of interest, in most of the selected groups, except large golden wires and CPU. Considering the higher ratio of metals to the total weight of these components, the acid content of the solution is not enough at a pulp density of 10-20%. So, a lower pulp density should be considered for treating this kind of component.

The weight percentage of solid residue after the chemical attack was calculated for all samples of both providers of SEAT and POLLINI. Table 26 and Table 27 show the weight percentage of solid residue for SEAT and POLLINI, respectively.

Table 26: Weight percentage of solid residue after chemical attack for different components of the main board of SEAT 350 LEON II.

Components	Initial weight (g)	Final solid weight (g)	wt. % of solid residue
Blue connector	7.424	5.455	73.48
Display connector	0.585	0.41	70.09

Small PCB	0.54	0.331	61.30

Table 27: Weight percentage of solid residue after chemical attack for six selected groups of components (POLLINI).

Groups of components	Initial weight (g)	Final solid weight (g)	wt. % of solid residue
Display connectors	3.743	2.477	66.18
small Golden wires	1.308	0.104	7.95
Black connectors	18.172	14.28	78.58
LCD pins	2.224	0.135	6.07
large Golden wires	3.092	0.305	9.86
CPU	5.414	1.938	35.80

5.2. Leaching optimization

Regarding characterization of each component (Table 13) and the availability of dashboards provided by SEAT and POLLINI, it was concluded that an optimization leaching experiment can be performed by a mixture of small golden wires, large golden wires, display connectors and CPU detached from POLLINI dashboards. Black connectors were ignored in this experiment, due to their insufficient content of precious metals (Table 13).

Chemical characterization of the mixture of components is shown in Table 28. It can be seen that sufficient amount of precious metals exist in this mixture which means it can be treated by GR2 process. Hence, the obtained mixture was treated by GR2 process with two stages of leaching. The results are shown in Table 29.

Table 28: Chemical characterization of the mixture of different components of the main board (POLLINI).

		Mixture: Display connector, large and small Golden wires, CPU
g/ton	Ag	913
	Au	248
	Pd	63
	Ti	9593
	Zn	3015
	Pb	55
	Cr	1359
	Fe	6338
%wt.	Cu	38.06
	Ni	1.70
	Sn	2.49

Table 29: Metal recovery in each stage of leaching for the mixture of different components of the main board (POLLINI).

Groups of components	Elements	Extraction yield (%)		Remained value in solid residue	Total
		1st stage of leaching	2nd stage of leaching		
Mixture: Display connector, large and small Golden wires, CPU	Ag	64.08	12.20	23.72	100
	Au	34.94	12.43	52.63	100
	Pd	37.46	23.33	39.21	100
	Ti	3.98	3.49	92.53	100
	Zn	34.90	21.99	43.11	100
	Pb	15.61	4.04	80.35	100
	Cr	31.78	9.73	58.49	100
	Fe	31.06	9.57	59.28	100
	Cu	36.15	23.19	40.66	100
	Ni	49.41	6.37	44.22	100
	Sn	92.09	0	7.91	100

In Figure 8 is shown the final solid residue of a mixture of components after leaching operations.

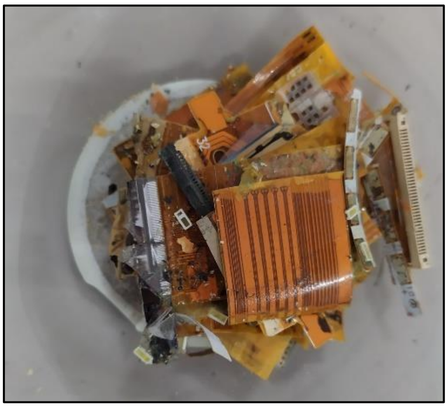


Figure 8: Solid residue of mixture of components after leaching (material from Pollini dashboards)

Table 29 shows that even with two stages of leaching about half of the gold is remained undissolved. As stated before, the reason for low leaching efficiency is probably the presence of high value of other elements these components which use much more reagents and reduces reagent's concentration in the solution. High content of these elements can also interfere the dissolution of gold. Improper immersion of small PCB in the solution can also be considered as the other reason for low recovery of precious metals during leaching. Therefore, it seems increasing liquid to solid ratio can improve leaching efficiency of precious metals by overcoming the above-mentioned problems.

Weight percentage of solid residue after chemical attack was calculated for the mixture of components. As can be seen, after complete dissolution of metals about 53% of initial weight of waste is remained (Table 30).

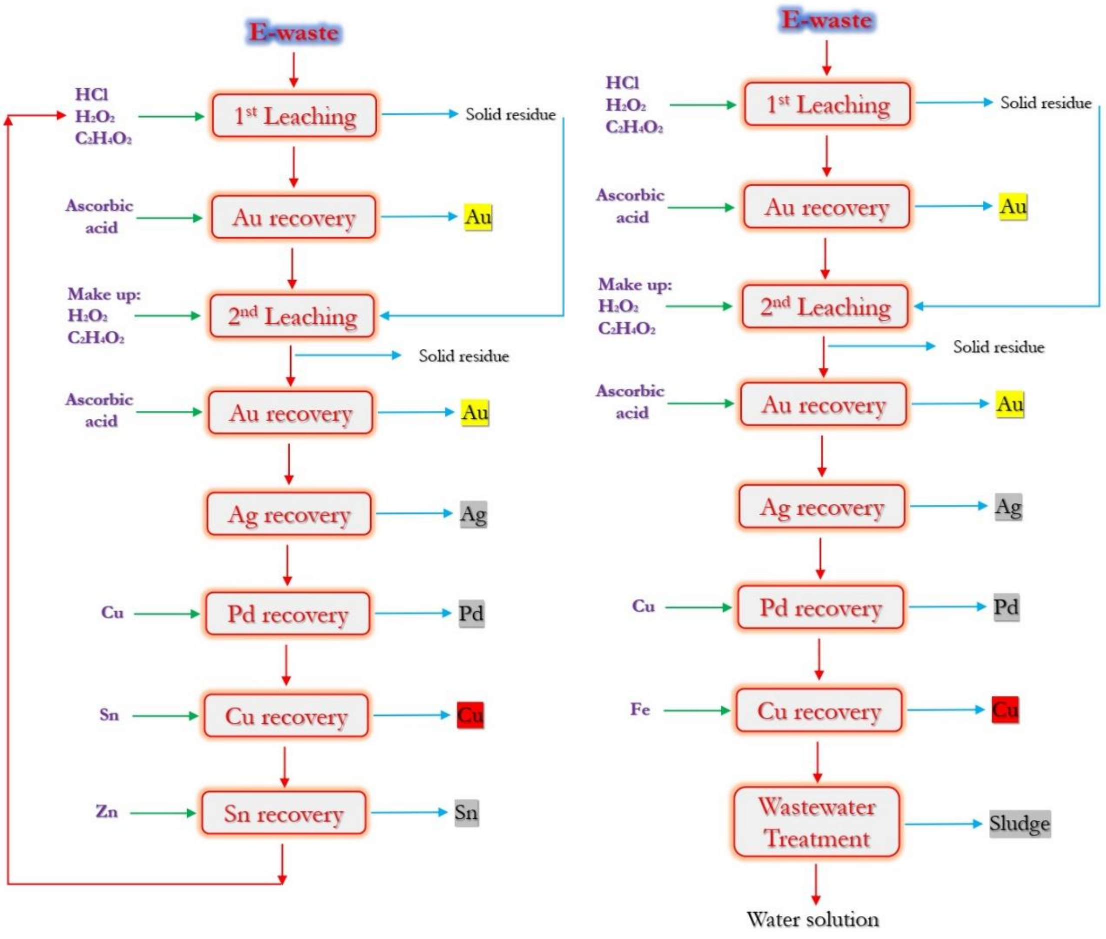
Table 30: Weight percentage of solid residue after chemical attack for the mixture of different components of the main board (POLLINI).

Components	Initial weight (g)	Final solid weight (g)	wt. % of solid residue
Mixture: Display connector, large and small Golden wires, CPU	10.883	5.734	52.69

5.3. Selective metal recovery

In this section selective metal recovery are investigated. Four tests (No. 1-4) of metal recovery were carried out on the solutions obtained in previous leaching sections. Based on GR2 process Au, Ag, Pd, Cu and Sn can be recovered selectively in different stages. Hence, the selected tests underwent these recovery stages. It should be mentioned, due to low concentration of Pd in solutions, Pd recovery stage carried out only in test No. 1. Sn recovery was performed in two steps in all tests, except test No. 4 in which, Cu recovered by adding Fe and Sn recovery was eliminated.

The first solution obtained by mixing leaching solutions of six selected groups of components of 9 dashboards provided by POLLINI (Table 29). Two separate routes of recovery experiments were performed using this solution. The first route carried out by selective metal recovery of Au, Ag, Pd, Cu and Sn considering the purpose of solution recirculation to the leaching stage (test No.1). The second route was performed to investigate the final solution’s composition for disposal purposes of solution and wastewater treatment (test No. 2). In this test Cu is recovered by adding Fe, at the final stage by omitting Sn recovery stage. Figure 8 illustrates two flowcharts for two possible recovery routes.



(a) (b)

Figure 9: Two flowcharts for selective recovery of metals of interest in two possible routs: a) with the possibility of recirculation of solution, b) for disposal purposes in which, final solution is sent to wastewater treatment stage.

The second solution for the recovery experiments obtained by mixing leaching solutions of different components of the main board of SEAT 350 LEON II (Table 24), in which only leaching solution of display connector and small PCBs were mixed (test No.3). Finally, the third solution obtained after leaching of the mixture of different components of the main board (POLLINI) in previous leaching optimization section (Table 29).

The results of metal recovery in four tests are presented in Table 31. In this table recovery percentages for all elements of interest are calculated in each recovery stage, and total metal recovery for each element is calculated considering all metal recovery stages. The initial and final concentration of elements in the solution are also presented in the last two columns of the table (Table 31).

In these calculations, there is a problem for calculating the recovery percentages of Cu, Sn, Zn and Fe. For example, in Cu recovery stage, Sn should be added to the solution for Cu precipitation. Therefore, Sn concentration is increased respect to its initial concentration in solution, which makes problem in recovery calculations. This problem is also occurred for Cu (in Pd recovery), Zn (in Sn recovery) and for Fe (for Cu recovery in test No. 4). So, for this situation the calculations were performed based on the explanations that given below the table. The related cells were highlighted in the table.

Table 31: Selective metal recovery results in different stages for 4 selected solution of leaching process (Test No. 1-4).

Recovery tests numbers	Elements	Recovery yield in each recovery stage (%)								
		Au recovery stage	Ag recovery stage	Pd recovery stage	Cu recovery stage	1st Sn recovery stage	2nd Sn recovery stage	Total recovery (%)	Initial conc. (mg/l)	Final conc. (mg/l)
Test No.1: Mixed solution of six selected groups of components (POLLINI)	Ag	0	22.43	17.81	59.05	0.34	0.16	99.79	36.61	0.1
	Au	45.08	0	42.52	0.62	7.64	1.90	97.77	0.61	0.02
	Pd	0	2.73	0	93.84	3.43	0	100	2.73	0
	Ti	10.21	5.64	12.62	12.28	13.26	12.76	66.77	25	11.84
	Zn	0	0	13.51	11.54	0	0	25.05**	3777	47165
	Pb	4.54	4.98	13.97	7.18	22.23	23.84	76.74	63	18
	Cr	0	0	14.92	10.68	14.95	16.06	56.61	122	71
	Fe	0	3.38	14.56	9.61	14.33	15.88	57.75	536	303
	Cu	1.95	5.85	0	96.42	3.55	0.01	99.99*	21365	2
	Ni	0	0.55	15.23	10	39.17	9.58	74.53	52301	17684
	Sn	8.75	0	9.26	0	69.35	23.31	92.65*	1936	2086
Test No.2: Mixed solution of six selected groups of components (POLLINI) (Fe addition)	Ag	39.49	6.35	-	52.40	-	-	98.25	64.92	0.93
	Au	34.84	11.20	-	53.96	-	-	100	0.77	0
	Pd	0	6.26	-	93.74	-	-	100	2.73	0
	Ti	4.28	9.50	-	21.41	-	-	26.20	25	14.71
	Zn	2.16	7.88	-	12.07	-	-	22.12	3595	2248
	Pb	1.42	58.58	-	5.76	-	-	65.76	53	33
	Cr	4.39	9.56	-	12.04	-	-	25.99	136	81
	Fe	4.24	8.47	-	0	-	-	12.71	563	11744
	Cu	3.17	8.94	-	87.84	-	-	99.95	20129	5.4
	Ni	4.30	8.89	-	9.75	-	-	22.95	50511	31255
	Sn	0	11.51	-	11.01	-	-	22.52	1977	1231
Test No.3: Mixed solution of different components of SEAT 350 LEON II	Ag	4.41	37.53	-	29.21	3.67	10.64	85.46	27	3.6
	Au	89.31	6.75	-	3.50	0.11	0.03	99.70	10	0.03
	Pd	0	0	-	0	0	0	0	0.2	0.06
	Ti	2.49	13.49	-	13.58	14.20	9.94	53.70	522	223
	Zn	48.05	0	-	0	0	0	48.05**	15	4246
	Pb	0	0	-	0	0	0	0	0.6	0.6
	Cr	0	0	-	0	0	0	0	0.8	0.3
	Fe	18	8.03	-	10.68	9.73	10.58	56.99	25	10
	Cu	0	13.04	-	13.44	13.36	11.45	51.29	2388	1052
	Ni	0	16.75	-	11.26	12.42	11.07	51.50	51425	22610
	Sn	0.97	11.57	-	0	11.56	16.15	27.71*	665	1772
Test No.4: Solution of optimization leaching test of mixed components (POLLINI)	Ag	3.30	0	-	87.07	2.90	5.07	98.34	72.23	0.96
	Au	64.67	14.64	-	19.36	0.59	0.73	100	5.91	0
	Pd	10.29	2.95	-	83.87	2.89	0	100	3.78	0
	Ti	33.25	5.12	-	1.91	5.24	5.09	50.61	72	28
	Zn	67.60	0	-	6.37	0	0	73.97**	169	26083
	Pb	47.20	0	-	0	0	0	47.20	2	1.3
	Cr	0	0	-	2.89	7.49	9.29	19.68	54	35
	Fe	0	0	-	4.08	7.85	7.48	19.42	247	160
	Cu	5.24	6.24	-	83.42	0	5.09	99.99	22552	0.92

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101003587

	Ni	6.57	6.61	-	2.96	14.75	8.41	39.31	90244	43947
	Sn	0	3.68	-	0	38.37	37.60	75.98*	2316	3878

*Total recovery value calculated based on the concentration of the metal in solution, after added values of Cu and Sn for Pd recovery and Cu recovery, respectively.

** Total recovery value calculated based on the concentration of zinc in solution, before adding Zn for Sn recovery.

5.3.1. *Gold recovery*

Gold recovery is performed by reduction with ascorbic acid, according to the following reaction:

$AuCl_3 + 1.5\ C_6H_8O_6 \rightarrow Au + 3\ HCl + 1.5\ C_6H_6O_6$

A proper amount of ascorbic acid added to all solution to have 5g/l ascorbic acid in solution. It should be mentioned, 5g/l of citric acid was added to the solutions to react with the remained H_2O_2 in the solution before the addition of ascorbic acid. Table 31 shows that Au recovery is acceptable for test No. 3 and No. 4, while it is not satisfying for test No. 1 and test No. 2, which both performed on the same solution obtained from mixing the leaching solutions of the components (POLLINI). The reason for low Au recovery in these tests, probably, is the very low Au concentration of the initial solution (0.6 ppm). So, by increasing Au concentration in the solution (removing the components poor in gold content in the leaching stage), it is expected gold recovery be increased, same as test No. 3 and No. 4.

5.3.2. *Silver recovery*

Silver recovery is performed by mixing the washing water (30% of leaching liquor) and the primary solution, and colling down the solution to 5 °C immediately, after Au recovery stage. According to the results of Table 31, Ag recovery stage is not successful for recovering silver in all four tests. It seems Ag particle size is in the nanometric scale and silver nanoparticles are passed through the filter. So, the filtration method should be changed to capture silver nanoparticles.

5.3.3. *Palladium recovery*

Palladium recovery is carried out by chemical cementation by adding copper metal powder into the solution as follows:

$PdCl_2 + Cu \rightarrow CuCl_2 + Pd$

Copper addition is 6 g/l. As stated before, Pd measurements are associated with some uncertainty, due to its low concentration in the solutions and interferences with other elements during spectrometry. So, it seems there is no Pd in leaching solution. Hence, Pd recovery was only carried out in test No. 1. The results shows that Palladium recovery is zero in Pd recovery stage (Table 31), probably due to its very low concentration in solution and measurements error.

5.3.4. *Copper recovery*

Copper recovery is performed by chemical cementation by adding tin metal powder into the solution as follows:

$CuCl_2 + Sn \rightarrow SnCl_2 + Cu$

Sn addition is 80 % of the stochiometric value. As it can be seen in Table 31, copper recovery stage is successful in all tests with high recovery percentages, except test No. 3, in which only 13% of Cu is precipitated by adding Sn to the solution. Table 31 also shows that the total Cu recovery percentage is near to 100% which leads to a very low concentration of Cu in final solution.
In test No. 2 copper recovery was carried out by adding iron metal powder into the solution to have Cu cementation as follows:

$CuCl_2 + Fe \rightarrow FeCl_2 + Cu$

Iron addition is 150 % of the stochiometric value. As stated before, the test's purpose was to investigate the final solution's composition for disposal purposes of solution and wastewater treatment. It is obvious that the final solution contains high concentration of iron (Table 31). As can be seen about 80% of Sn remained in the final solution.

5.3.5. Tin recovery

Tin recovery is performed by chemical cementation by adding zinc metal powder into the solution as follows:

$SnCl_2 + Zn \rightarrow ZnCl_2 + Sn$

According to GR2 process, zinc addition should be 170 % of the stochiometric value. In all 4 tests of recovery, Sn recovery was performed in two steps to have an acceptable recovery percentage of Sn. In each stage 170% and even more zinc (up to 270% of the stochiometric value) was added. Nevertheless, Sn recovery is low in test No. 3 and test No. 4 (Table 31). A probable reason for low recovery of Tin is the agglomeration of Zn particles while adding to the solution, which reduces the reaction efficiency.

6. Process analysis

In this section, mass balances of the optimized hydrometallurgical processes were described. Then, all the outputs were characterized in order to define the economic sustainability of the process. Two processes were analysed according to the scheme shown in Figure 1, section 3.3. In the following subsections, the process analysis was carried out for GDR1 on the powders of PCBs and for GDR2 on the components of PBCs.

6.1. Powders (GDR1)

The flow sheet of the modified GDR1 is shown in Figure 10. This process is composed of 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 occur. This selective leaching is very helpful in separating metals already in the leaching section, allowing their efficient recovery. Tin is precipitated by flocculation with the aim of polyamine in the form of metastannic acid that can be thermally treated to obtain tin oxide as a final product. Copper remains in the solution after filtration and is recovered by electrodeposition. The second pregnant solution after the thiourea leaching undergoes the recovery of gold and silver by electrodeposition, which based on the experimental tests, cannot take place selectively. Therefore, is to be considered a refining step aimed at dissolving silver from the gold-silver alloy to increase gold purity. Silver can be recovered from the acid solution as chloride.

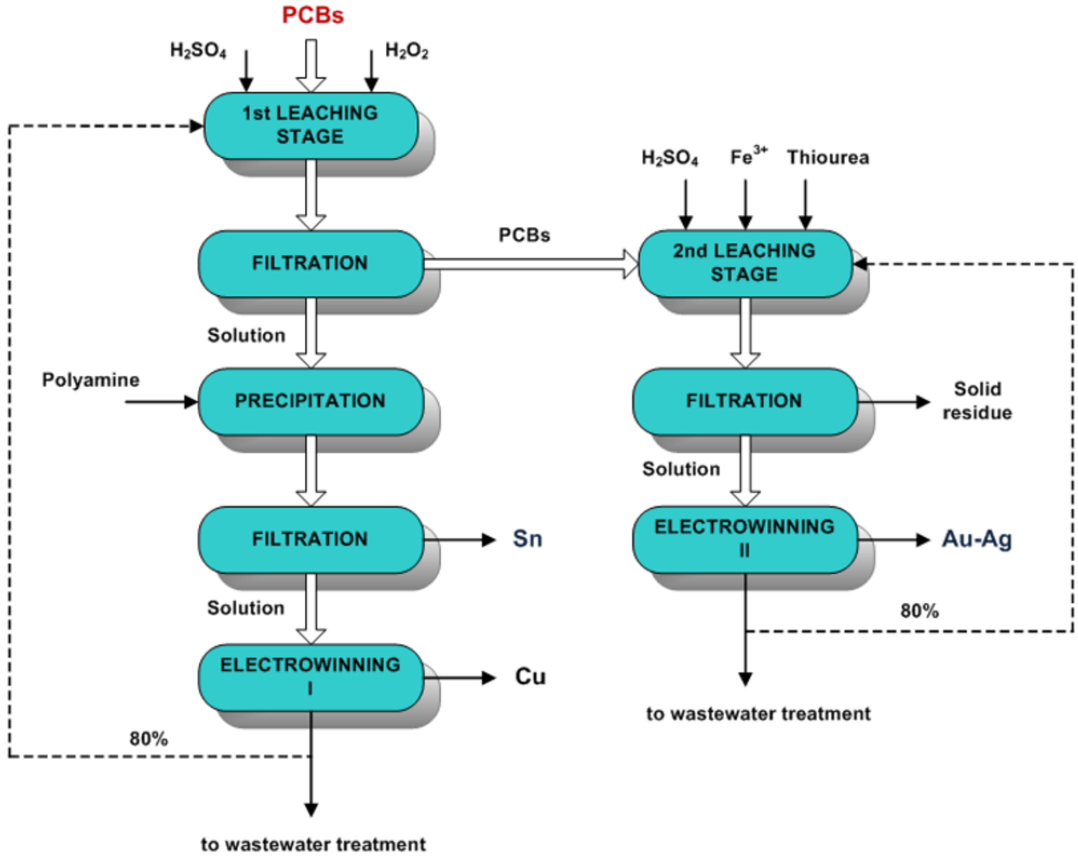


Figure 10: GDR1 hydrometallurgical recycling process flow sheet for the treatment of PCBs powders.

In addition, it should be considered that with the aim of minimizing wastewater production and chemical consumption, the first step of leaching of base metals, which includes three leaching steps by hydrogen peroxide and sulfuric acid, was studied to be conducted by a counter-current scheme (Figure 2). A summary of the experimental results was reported (Table 32).

Table 32: Summary of the obtained results for GDR1 process.

stage	Recoveries			
	Au	Ag	Cu	Sn
1st leaching stage			95%	96%
2nd leaching stage	70%	89%		
Sn precipitation				89%
Cu electrowinning			97%	
Au-Ag electrowinning	85%	55%		

Therefore, the dissolution of 95% of Cu and 96% of Sn occurred during the 1st leaching stage (multi-stage counter-current leaching), then the solid was subject to a 2nd leaching stage, and the dissolution of 70% of Au and 88% of Ag was achieved. From the first solution was recovered

89% of Sn by precipitation, and then 97 % of Cu by electrowinning. The recovery of Au and Ag from the second solution was 85% and 55%, respectively.

In Table 33, based on the experimental lab-scale tests, a mass balance was described considering all the inputs and outputs of the GDR1 hydrometallurgical process; the mass balance is referred to the treatment of 1 ton of PCBs.

Table 33: Mass balances for the treatment of 1 ton of PCBs powders with GDR1 process.

Input	kg	Output	kg
Solid (more details in Table 33)	1000.0	Dry solid residue	783.0
H_2SO_4 (50 % w/v)	2719.4	Wastewater 1	6899.3
H_2O_2 (30 % w/v)	1477.9	Wastewater 2	8375.2
Thiourea	164.4	Tin oxide	11.24
Ferric sulphate	184.8	Copper	178.3
Polyamine (10 % w/v)	19.1	Gold-Silver	0.189
Water for 1st leaching stage	4280.0	Humidity	511.2
Water for 2nd leaching stage	7764.8	-	-
Total input	17610.4	**Total output**	16758.4
Experimental error 4.8%			

Concerning the outputs, the humidity is referred 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. Wastewater 1 is the sulfuric acid solution after the base metals counter-current leaching, from which tin and copper have been recovered. Wastewater 2 instead is the thiourea solution from which gold and silver have been recovered by electrodeposition. Wastewater densities were 1.15 g/cm^3 and 1.07 g/cm^3, respectively. About the products, 11.24 kg of tin oxide is recovered after metastannic acid oxidation at 650 °C, 178.3 kg of copper is recovered by electrodeposition, and the mixture of gold-silver alloy, also named dorè, is recovered after electrodeposition. A leaching stage can be performed by using nitric acid to dissolve silver and leave gold metal as a solid residue to separate gold and silver. Then, adding hydrochloric acid or sodium chloride can precipitate silver nitrates as silver chlorides.

PCBs powders' input characterization is shown in Table 34. The powders are obtained after removing some components (Table 2) and subsequent grinding up to 2 mm.

Table 34: Solid input characterization (powders of PCBs)

Input – PCBs powders (below to 2 mm after removal of some components)			
Metals (ICP-OES analysis)		C-H-N-S analysis	
Cu, wt. %	19.1	Carbon wt. %	22.62
Al, wt. %	2.46	Hydrogen wt. %	1.62
Sn, wt. %	1.01	Nitrogen wt. %	0.34
Ni, wt. %	0.29	Sulfur wt. %	0.30
Fe, wt. %	0.28		
Ti, wt. %	0.18		
Zn, wt. %	0.11		

Ag, g/t	273.3
Au, g/t	94.2
Zr, g/t	33.7
Pd, g/t	27.5

The previous table showed the main metals detected in the PCBs powders, identified by chemical attacks and subsequent quantitative ICP-OES analysis on the obtained solution. In addition, also C-H-N-S elemental analysis was provided. Concerning metals, almost all are present in their metallic form or as alloys. Aluminium, instead, is present both in metallic form and as oxide (Al_2O_3) in the ceramic parts. The remaining parts of the powders of PCBs are composed, as average values, of 30% plastics and 40% of fiberglass impregnated with epoxy resins. Epoxy resin content is about 8%, and calcium oxide could be in the range of 5-10%, also present in the ceramic part. SiO_2 is generally at least 15%, and low content of about 0.5% of MgO could also be present [5].

The process outputs have been characterized to evaluate their management in case of disposal or treatment and to define the selling price in the case of products of industrial interest. The outputs are below listed:

a. dry solid residue
b. wastewater 1 (from the base metals leaching stages)
c. wastewater 2 (from the precious metals leaching stage)
d. tin oxide
e. copper
f. gold-silver

Dry solid residue

The dry solid residue is the powder of PCBs subjected to the leaching operations to dissolve base and precious metals. The obtained amount is 783 kg for 1 ton of treatment; the residual metal fraction is about 4-5% wt., detected by the solid residue chemical attack. In Table 34, the residual metal contents were reported.

Table 35: Dry solid residue metal characterization

Dry solid residue metal characterization	
Al, wt. %	2.57
Cu, wt. %	1.07
Ti, wt. %	0.23
Fe, wt. %	0.15
Sn, g/t	464
Ni, g/t	729
Zn, g/t	435
Zr, g/t	70.3
Ag, g/t	34.9
Au, g/t	20.4
Pd, g/t	5.3

During the leaching operations, the metal fraction is essentially affected, while the residual parts of the PCBs, such as fiberglass and plastic, remain in the solid residue.

Wastewater 1

Wastewater 1 is the spent solution that, according to Figure 9, is obtained from the leaching system composed of sulfuric acid and hydrogen peroxide to dissolve base metals. After the leaching operations, performed in counter-current flow, from this solution are recovered tin by precipitation and copper by electrodeposition. According to reaction 4, which occurs during the electrodeposition, it can be observed how the free acidity increases in the solution due to the reaction that takes place at the anode.

$$Cu^{2+} + SO_4^{2-} + H_2O \rightarrow \ Cu^0 \ + 0.5\ O_2 + 2H^+ + SO_4^{2-} \qquad \text{(equation 4)}$$

Experimental tests by adding soda to the solutions were carried out to determine the titration curve before and after electrowinning to calculate the concentration of sulphuric acid and assess whether it actually increases due to electrowinning. Results showed that before the electrodeposition, H_2SO_4 concentration was 1.27 mol/L, while after recovering the copper by electrowinning increased up to 1.58 mol/L. Whereas the concentration of H_2SO_4 used for leaching base metals is 1.8 mol/L, this result allowed the reusing of the solution to the leaching operations to reduce sulfuric acid consumption. The experimental tests were carried out by recycling 80% v/v of this solution for the treatment of a new cycle of PCBs powders; hydrogen peroxide, used as an oxidant agent, has to be completely added as it is totally degraded during leaching reactions.

The remaining 20 %, the analysis of which is reported in Table 36, must be purged.

Table 36: Wastewater 1 composition

Wastewater 1 composition	
Sulfuric acid	1.58 mol/L
pH	< 0.5
Cu	819 mg/L
Al	378 mg/L
Fe	227 mg/L
Ni	205 mg/L
Sn	110 mg/L
Zn	12 mg/L
Ti	< 5 mg/L

At this stage, the preliminary economic analysis considered the disposal of this wastewater by an external company at a cost of 130 €/m^3.

However, in the case of the realization of an industrial plant, a section for wastewater treatment will certainly have to be included to reduce the operative costs and environmental sustainability in water reuse. Wastewater mainly consists of copper sulphates, the treatment could include chemical cementation by adding iron metallic powders to recover copper, then neutralization can be performed by adding $Ca(OH)_2$ up to pH 8-9 in order to precipitate the residual metal content as sludges. Sulphates concentration should be detected to discharge into sewer or reuse this water. Figure 11 shows the wastewater process treatment.

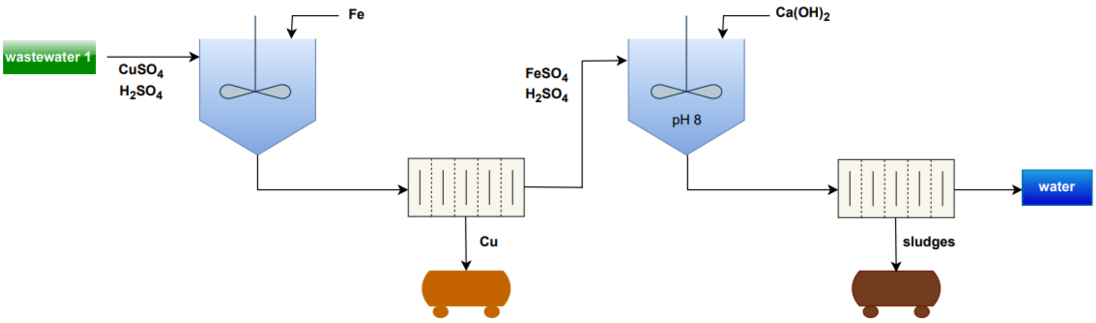


Figure 11: Wastewater 1 treatment of 20 % v/v for each cycle.

Wastewater 2

Wastewater 2 is the spent solution that, according to Figure 10, is obtained from the leaching system composed of thiourea, ferric sulphate and a low concentration of sulfuric acid, to dissolve precious metals. After the leaching operation, the leach liquor solution is subjected to gold and silver recovery by electrodeposition.

A partial regeneration of thiourea was observed after the electrodeposition, therefore studies were performed by recycling 80% v/v of this solution for the treatment of the subsequent cycle of the process. The reactions that occur during electrodeposition are shown below:

$$(Au(CS(NH_2)_2)_2)^+ + e^- \rightleftarrows Au^0 + 2\,CS(NH_2)_2 \qquad \text{(equation 5)}$$

$$NH_2NHCSSCNHNH_2 + 2H^+ + 2e^- \rightleftarrows 2\,CS(NH_2)_2 \qquad \text{(equation 6)}$$

In the first reaction is shown the reduction of the gold-thiourea complex and in the second reaction formamidine disulfide, resulting from the thiourea degradation that partially occurs during the leaching, is reduced, by contributing to partial regeneration of thiourea. In Table 37 is shown the composition of wastewater 2.

Table 37: Wastewater 2 composition

Wastewater 2 composition	
thiourea	19 g/L
sulfuric acid	0.2 mol/L
pH	1.0
Fe	4.7 g/L
Cu	118 mg/L
Al	78 mg/L
Ti	18 mg/L
Ag	16 mg/L
Sn	8 mg/L
Ni	5 mg/L

Figure 12 shows the wastewater 2 process treatment. For each cycle, 20% v/v of the spent solution is sent to this treatment, while most, 80% v/v, is recycled for leaching precious metals in the next treatment cycle. Based on the high concentration of iron in wastewater 2, only a low dosage of the $FeSO_4$ Fenton reactive is necessary. The quality of the obtained water has to check to evaluate if can be recycled in the hydrometallurgical process or can be sent to the sewage.

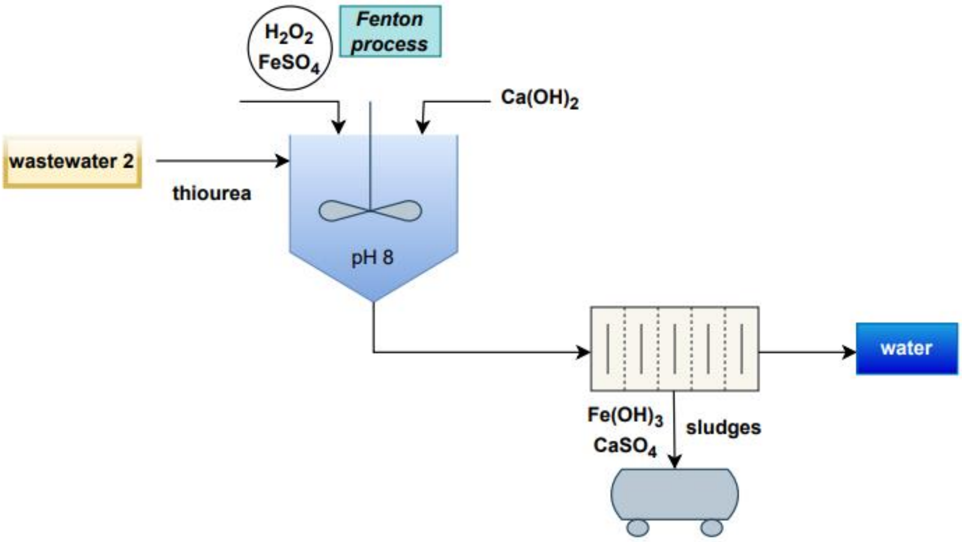


Figure 12: Wastewater 2 treatment of 20 % v/v for each cycle.

Tin oxide

Tin oxide product was obtained after recovery of tin from the first leach liquor solution by precipitation with the use of polyamine. After filtration, metastannic acid is obtained. This product is thermally treated at 650 °C to obtain tin oxide with the following composition, as shown in Table 38.

Table 38: Tin oxide composition

Product	SnO_2 %	CuO %	traces
Tin-oxide	97.4	2.3	Polyamine, Zn, Ni, Al

Copper

Copper was obtained by electrodeposition, after that tin was recovered from leach liquor solution obtained by the first leaching step of PCBs powder, the base metals dissolution. The grade of obtained copper was about 99 % with different metal impurities as shown in Table 39.

Table 39: Copper composition

Product	Cu %	Fe %	Ni %	Zn %	Al %
Copper	98.7	0.55	0.37	0.32	0.22

The sum of the content of the elements consisting of the copper product slightly exceeds 100 % wt. due to experimental errors.

Gold-silver

Based on the small quantities treated at the lab-scale, the composition of the gold-silver product was not determined. However, the gold and silver content was estimated by considering the decrease in their concentrations in the solution at the end of the electrodeposition. The product estimation composition is 29 % of gold grade and 71 % of silver grade. It is a typical composition of a product named 'dorè'.

Selective separation of gold from silver can be obtained by performing a nitric acid leaching stage that aims at dissolving only silver. Although the use of nitric acid is not environmentally sustainable due to the production of NOx gaseous emissions, in this case, given the very low quantities to be treated, 0.189 kg of gold-silver product per ton of PCBs powders, is a route that can be followed. Then, silver is recovered from the solution in the form of chlorides by adding hydrochloric acid or sodium chloride, while a gold concentrate remains in the solid residue of nitric acid leaching.

Table 40 summarizes the distribution of various elements for each process output. The most present elements in the initial sample are considered.

Table 40: Distribution of various elements in the process outputs

Items	Cu, %	Sn, %	Al, %	Fe, %	Ti, %	Ni, %	Zn, %
Solid input	100	100	100	100	100	100	100
Tin oxide	< 1	89	1	0	0	8	10
Copper	92	< 0.5	2	35	0	23	52
Wastewater 1	3	7	12	23	1	47	7
Wastewater 2	< 1	< 0.5	3	0	1	2	0
Dry solid residue	4	4	82	42	98	20	31

Economic evaluations on the GDR1 recycling process are done based on the balance materials (Table 32), calculated by experimental lab tests, and referred to a treatment of 1 ton of powders from PCBs. Output characterization allowed us to estimate the wastewater and solid residue disposal cost. With regard to the useful products generated by the process, the grade of gold and silver chlorides could be evaluated with pilot scale tests since, at the lab scale, it is not possible due to the low amount of processed powders and, therefore, gold that is just over 1 mg. Table 41 shows the chemical costs for the treatment of 1 ton of PCBs powders.

Table 41: Chemical consumptions and costs for the treatment of 1 ton of PCBs powders.

Chemical	Amount, kg	Cost per unit, €/kg	Cost, €
H_2SO_4 (50 % w/v)	2719.4	0.13	353.5
H_2O_2 (30 % w/v)	1477.9	0.40	591.2
Thiourea	164.4	1.00	164.4
Ferric sulphate	184.8	0.30	55.4
Polyamine	19.1	1.00	19.1
Water	12084.8	0.0015	18.1
			1201.7€

The total cost of chemicals is 1201.7 €. Hydrogen peroxide contributes the most, accounting for almost 50 % of the total cost of chemicals. For this reason, the optimization tests were conducted to minimize the consumption of hydrogen peroxide by adopting factorial experimentation. In the GDR1 process, according to the patent, the incidence of hydrogen peroxide was even higher. The pie chart shows the contribution of each chemical to the total cost of chemicals (Figure 13).

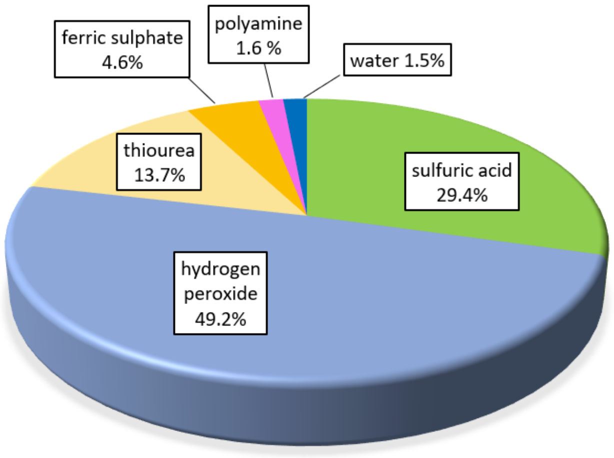


Figure 13: Contribution of each chemical on the total cost of chemicals.

Regarding energy consumption, the GDR1 process for the treatment of PCBs powders can be developed in a plant that requires the following energy consumptions: stirring for the leaching operations and for the preparation of the solutions, pumps to discharge the chemical reactors and to separate the leach liquor from the solid residue, the furnace to oxidize the metastannic acid that needs to be conducted at 650 °C for 1 h, and the energy consumption for the electrodepositions, that was 2.1 kWh/kg for the copper and 10 kWh/kg for the precious metals. Table 42 shows the energy consumption for each specific operation.

Table 42: Energy consumption

Operation	kWh
Stirring	27
Pumps	32
Furnace for tin refining	123
Cu electrowinning (2.1 kWh/kg)	374
Au-Ag electrowinning (10 kWh/kg)	1.9
	557.9 kWh

Operative costs, OPEX (operative expenses), in addition to the cost of chemicals and the cost of energy consumption, also include the costs for the disposal of process outputs such as wastewater and solid residue.

In Table 43 A is shown a scenario in which OPEX has been reported, and no recycling of solutions for new treatment cycles is considered. In this case, the significant impact of the cost of wastewater disposal, which amounts to almost 50 % of the total operating costs, is quite obvious.

Table 43 A: OPEX for the treatment of 1 ton of PCBs powders without recycling of spent solutions.

Item			Cost, €/ton of PCBs powders
Chemicals	details are reported in Table 33		1201.7
Energy consumption	kWh	€/kWh	200.8
	557.9	0.36	
Wastewater	m^3	€/m^3	1792.7
	13.79	130	
Solid residue	kg	€/kg	469.8
	783	0.60	
			3669.7€

For this scenario, the OPEX is 3669.7 €/ton of PCBs powders.

Then, a new scenario concerns experimental studies, in which 80 % of the spent solutions from the first and second leaching steps are recycled, and therefore for each cycle is sent to treatment, only 20 % of each of the two wastewaters. For this scenario with the recycling of spent solutions, OPEX is reported in Table 43 B. For the new scenario, the OPEX is 2231.1 €/ton of PCBs powders.

Table 43 B: OPEX for the treatment of 1 ton of PCBs powders with 90% recycling of spent solutions.

Item			Cost, €/ton of PCBs powders
Chemicals	details are reported in Table 33		1201.7
Energy consumption	kWh	€/kWh	200.8
	557.9	0.36	
Wastewater	m^3	€/m^3	358.8
	2.76	130	
Solid residue	kg	€/kg	469.8
	783	0.60	
			2231.1€

Regarding revenues, currently, the price of metals and salts is considered. In any case, this phase is critical because it is totally dependent on the purity obtainable. Purities must be confirmed and determined again after the scale-up of the process. In addition, the price of salts can generally also depend on agreements that are made with specific companies that use them. Table 44 shows revenues for the treatment of 1 ton of PCBs powders.

Table 44: Revenues from the treatment of 1 ton of PCBs powders.

Products	Production	selling price	revenue, €
Tin-oxide	11.24 kg	12.9 €/kg	145.0
Copper	178.3 kg	7.5 €/kg	1337.3
Gold	54.81 g	58 €/g	3179.0
Silver chloride	178.5 g	0.48 €/g	85.7

	4747.0 €

Based on these considerations, the process revenue is 4747 €/ton. Therefore, subtracting OPEX, you have a **2215.9 €/ton profit**. For a more detailed economic analysis, pilot-scale tests will allow us to estimate the revenues in a certain way and to define the profit margin from the GDR1 process on this material. Moreover, by defining a capacity of a potential industrial plant, CAPEX can be calculated, as well as economic performance indicators of the process such as the earnings before interests, taxes, depreciation, amortization, the payback time, and the return on investment.

6.2. Components (GDR2)

In the following a complete mass balance for the mixture of components are presented, according to the flowsheet in Figure 9-a. The mass balance was performed based on the optimization leaching test in section 5.2, considering the chemical analysis of the mixture of components (POLLINI), and leaching solutions and recovery results (Table 28, Table 29, and Table 31). Table 45 shows the mass balance for the whole process and distribution of the elements in all outputs. It should be noted, mass balance for Sn and Zn is somehow different, because some amounts of Sn and Zn are added in Cu recovery and two stages of Sn recovery, respectively. So, recovery percentages for Sn are considered respect to initial value of Sn in e-waste, till the Cu recovery stage, and then it has been calculated respect to the added value of Sn, during and after Cu recovery stage. Accordingly, the same method of calculation was applied for Zn. So, Zn recovery percentages are considered respect to initial Zn content till the Sn recovery stages, and afterwards it has been calculated based on the added value of Zn in Sn recovery stages. Therefore, considering this aspect regarding the added values of Sn and Zn, and considering the remained values of Sn and Zn respect to initial values in e-waste, the total mass in final solution is calculated based on treatment of 1000 kg of e-waste, which is presented in Table 46 (sum of added values of Sn and Zn and remained values in solution). According to mass balance calculations and input values, it is estimated that the final volume of solution is about 8667 litres. So, the mass values in Table 46 should be considered in this volume.

Table 45: Mass balance for the whole process for optimization leaching test of mixed components (POLLINI).

		Recovery yield of elements in each stream respect to initial value in the e-waste (%)								
	Elements	Au recovery between 2 leaching stages	Final solid residue	Au recovery stage (Au concentrate)	Ag recovery stage (Ag concentrate)	Cu recovery stage (Cu concentrate)	1st Sn recovery stage (Sn concentrate)	2nd Sn recovery stage (Sn concentrate)	Final solution	Total value (%)
Test No.4: Solution of optimization leaching test of mixed components (POLLINI)	Ag	3.2	23.7	2.4	0	63.6	5	3.7	0	101.6
	Au	23.7	52.6	15.3	3.5	4.6	0.8	0.2	0	100.7
	Pd	1.3	39.2	6.1	1.7	49.9	2	0	0	100.2
	Cu	0.6	40.7	3.1	3.7	49	2.1	3	0	102.2
	Sn	0	7.9	0	3.4	11.8*	38.4*	37.6*	88.7**	100
	Fe	0.8	59.3	0	0	1.6	0.6	3	34.7	100
	Ni	0.2	44.2	3.6	3.7	1.6	4	4.7	38	100
	Zn	1	43.1	37.8	0	3.6	0.2*	0*	14.5**	100

	Cr	0.7	58.5	0	0	1.2	0.2	3.8	35.6	100
	Pb	0	80.4	9.3	0	0	0	0	10.3	100
	Ti	0.1	92.5	2.5	0.4	0.1	0.2	0.4	3.8	100

*Respect to the added value of Sn (or Zn)

** respect to initial value in the e-waste

Table 46: Total mass of elements in final solution, before recirculating to the new leaching stage.

Ag (kg)	Au (kg)	Pd (kg)	Cu (kg)	Sn (kg)	Fe (kg)	Ni (kg)	Zn (kg)	Cr (kg)	Pb (kg)	Ti (kg)
0	0	0	0	50.21	2.20	12.87	299.90	0.48	0.006	0.37

Chemical analysis of recovered solids after each stage was carried out by chemical attack and doing mass balance. The results are presented in Table 47. For Ag and Au concentrates, the chemical composition calculated based on a mass balance in solution, before and after recovery process, due to very low value of recovered solids. But for Cu and Sn concentrates a few amounts of solid was dissolved in aqua regia. As it can be seen, gold and silver percentages are very low in Ag and Au concentrates and copper is the dominant element in the composition (Table 47).

Table 47: Chemical composition of solids after selective recovery stages.

	Wt. %										
	Ag	Au	Pd	Cu	Sn	Fe	Ni	Zn	Cr	Pb	Ti
Au concentrate (between 1st and 2nd leaching)	1.09	2.20	0.03	90.12	0	1.83	2.92	1.17	0.37	0	0.27
Au concentrate (after 2nd leaching)	0.15	0.26	0.03	81.36	0	0	8.61	7.91	0	0.04	1.64
Ag concentrate	0	0.05	0.01	86.70	5.24	0	7.77	0	0	0	0.23
Cu concentrate	0.37	0.01	0.01	84.48	14.68	0.05	0.27	0.11	0.01	0	0
1st Sn concentrate	0.06	0	0	10.40	79.60	0.05	1.77	0.76	0	0	0.2
2nd Sn concentrate	0	0	0	0.02	87.64	0.03	0.40	0.92	0.01	0	0.01

Considering 1 ton of E-waste and having a pulp density of 15 %wt./v, the required reagents can be estimated as Table 48, considering the lab results. The mass balance for input and output streams are calculated according to the process (Figure 9-a), with two leaching stages and make-up of some chemicals. In addition to solid outputs, some portion of elements remained in the final solution, which their total value was calculated based on the data in Table 46 and represented in Table 48. Therefore, final solution should be treated suitably to remove these elements, before reusing for leaching or disposal purposes. It can be seen, there is a 2% difference (235.43 kg) between total input mass and total output mass, which is probably, due to the error in calculations and analysis.

According to Table 48 it is possible to estimate the cost of chemicals which are used for treatment of 1 ton of E-waste. The results are shown in Table 49.

Table 48: Mass balances for the treatment of 1 ton of mixed components (POLLINI).

Input, kg		Output, kg	
Solid	1000	1st Au concentrate	2.64
Water	2666	2nd Au concentrate	13.76
HCl (37%)	2400	Ag concentrate	15.45
H_2O_2 (30%)	1480	Cu concentrate	187.54
$C_2H_4O_2$ (99%)	700	1st Sn concentrate	89.84
Wash water after Au recovery	2000	2nd Sn concentrate	98.87
Sn powder	230	Final solid residue	526.88
Zn Powder	300	Final solution	9246
		Remaining elements in final solution	359.59
Total input	**10776**	**Total output**	**10540.57**
Experimental error (%)			2.2

Table 49: Chemical consumptions and costs for treatment of 1 ton of e-waste.

Chemical	Amount, kg	Cost per unit, €/kg	Cost, €
Water	2666	0.0015	4
HCl (37%)	2400	0.18	432
H_2O_2 (30%)	1480	0.35	518
$C_2H_4O_2$ (99%)	700	0.4	280
Sn powder	230	1.5	345
Zn Powder	300	2	600
			2179€

The total cost of chemicals for treating 1 ton of e-waste is 2179 €. The pie chart shows the contribution of each chemical to the total cost of chemicals (Figure 14). As it can be seen, about 56% of the total cost belongs to leaching reagents and the remaining 44% belongs to metallic powders of Zn and Sn used for cementation. It is obvious that the total cost of chemical reagents can be reduced significantly by recirculating the solution to the new leaching cycles.

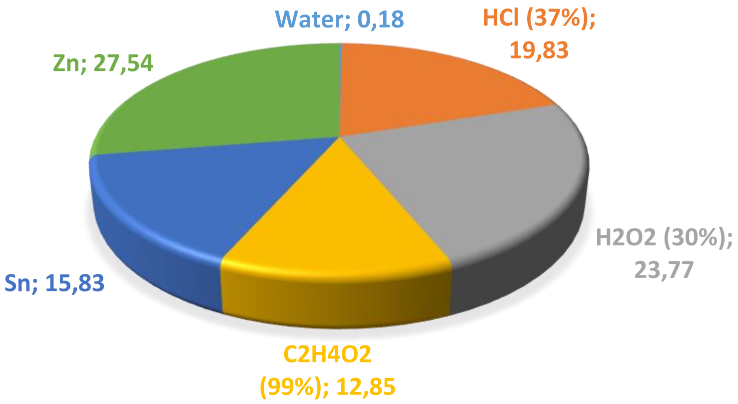


Figure 14: Contribution of each chemical on the total cost of chemicals.

Considering the impure products achieved in different stages of selective metal recovery (Table 47), it is not possible to calculate the revenues at this stage. Hence, some optimizations stapes should be taken in order to increase metal recovery and the purity of final products. Some suggestions are as follows:

a. Increasing leaching efficiency at two stages
b. Decreasing the concentration of base metals in the solution to increase the purity of final products (by a preliminary base metal leaching stage)
c. Increasing the recovery percentage of metals in selective precipitation stages

In order to achieve these goals, some critical issues encountered during the Gold-Rec 2 process should be addressed:

a. Selective recovery processes for gold and silver must be carried out in a rapid sequence in order to prevent the formation of complexes which prevent the precipitation of silver as AgCl.
b. Filtration of silver precipitates must be carried out with a filter capable of retaining even the AgCl particles of the order of a few nanometres.
c. The quantity of tin used for the copper precipitation (80% of the stoichiometric quantity) seems to be excessive and creates a purity problem and difficulty in recovering the tin in the subsequent operation due to the increase in the concentration in the solution.
d. The quantity of zinc used (70% in excess of the stoichiometric quantity) are not sufficient to effectively recover the tin in solution with a single step, and two step of Sn recovery was carried out, which needs to be optimized to reduce the amount of Zn in the solution and reduce the zinc consumption.

So, by increasing metal recovery and purity of final products, it would be possible to determine the revenues for each product and doing a suitable economic calculation.

7. Conclusions

In this study, various dashboards provided by partners (POLLINI and SEAT) were considered for recycling experiments on the lab scale. Each dashboard was disassembled to gain relevant PCBs. According to the different chemical compositions of various components in the electric boards, some components assumed to have more content of precious metals were detached from the bords to be treated by the patented process GOLD-REC 2 (GDR2), some components have been removed because inhibit the metals dissolution yields and cannot be recycled by hydrometallurgical processes, and the main electronic boards with remaining components were pulverized to a particle size of 2 mm and treated by the other patented process GOLD-REC 1 (GDR1).

Below are some comments regarding the GDR1 recycling process for the powders from PCBs:

a. Powders from PCBs, obtained after the removal of some components and pulverization, constitute about 70% wt. of the initial weight of PCBs.

b. Characterization of the powders as regards the metals contributing to the intrinsic economic values is as follows based on the different SEAT models:
   i. LEON II: Au 81.5 g/t, Ag 297.9 g/t, Pd 23.3 g/t, Cu 20.9 %, Sn 1.01 %
   ii. LEON III: Au 14.2 g/t, Ag 535.0 g/t, Pd 33.6 g/t, Cu 25.6 %, Sn 0.65 %
   iii. IBIZA IV: Au 94.2 g/t, Ag 273.3 g/t, Pd 27.5 g/t, Cu 19.1 %, Sn 1.01 %

c. Compared to the patent GDR1, the process has been optimized through factorial experimentation to maximize metals yields and reduce the consumption of hydrogen peroxide, which is the main cost item for chemicals. The obtained results showed that the base metals leaching must be carried out in three steps, one more than the patent, but with lower hydrogen peroxide consumption. Below is the concentration of chemicals used for each base metals leaching step and the metals extraction yields:
   i. First, second and third step: H_2O_2 (30% w/v) 10% v/v, H_2SO_4 1.8 mol/L.
   ii. Extraction yields: Au 70%, Ag 89%, Cu 95%, Sn 96%.
   Gold recovery cannot occur above 70%, probably due to the degree of liberation of gold particles. A preliminary thermal treatment was also carried out to release some organic compounds that could inhibit gold extraction but did not allow an increase in gold recovery.
   The palladium content in the initial powder is too low to hypothesize a recovery.

d. Other optimization studies of the process have been carried out to reduce the production of wastewater according to an MLD approach:
   i. The three stages of base metals leaching have been optimized by a counter-current flow that allowed to reduce further the chemical consumption and the production of wastewater. In fact, based on this scenario, sulfuric acid and hydrogen peroxide are only added in the third step of base metal leaching, while in the other two, only 50 % of hydrogen peroxide is added.
   ii. Both wastewater 1, generated from base metals leaching, and wastewater 2, generated from precious metals leaching, are recycled at 80% v/v for the treatment of the subsequent cycle. This has been adopted because a partial regeneration of thiourea occurs during the gold-silver electrodeposition and the increase of free acidity during the copper electrodeposition.

e. GDR1 modified/optimized hydrometallurgical process allowed to obtain the following outputs:
   i. Solid residue (78% wt. with respect to the input) is mainly composed of fiberglass and plastics. Regarding the metals, aluminium is the most present at 2.57% wt. and copper at 1.07% wt.
   ii. Wastewater 1 is a sulfuric acid solution with copper as the main impurity; a wastewater treatment was defined in order to recover copper and neutralize the solution by obtaining sludge of metals as hydroxides and water that, after the evaluation of sulphates concentration, could also be reused.
   iii. Wastewater 2 is a weak acid solution rich in thiourea and iron. Chemical oxidation treatment by Fenton process can be applied to obtain a sludge mainly composed of ferrous sulphate and water, of which it is necessary to check its quality to understand its reuse.
   iv. Tin-oxide at 97.4% of purity. The main impurity is copper, are also detected traces of zinc, aluminium, nickel, and polyamine.
   v. Copper at 98.7% of purity. Impurities are Fe 0.55%, Ni 0.37%, Zn 0.32%, Al 0.22%.
   vi. Gold-silver mixture that can be selectively separated after nitric acid leaching. Gold remains as a solid residue, and silver is dissolved and then recovered as chlorides by adding sodium chloride or hydrochloric acid.

f. Mass and energy balances are described and allowed to evaluate the economic sustainability of the optimized process. The preliminary economic analysis was conducted for the treatment of 1 ton of PCBs powders.
   i. Chemical costs are 1201.7€/ton.
   ii. The OPEX, also including energy consumption and wastewater/solid management, is 2231.1€/ton.
   iii. Revenues are 4747.0 €/ton, this value is closely related to the output purities. A more certain value can be obtained by pilot scale tests.
   iv. The profit by adopting GDR1 modified/optimized process for the treatment of 1 ton of PCBs powders is 2215.9 €/ton.

g. GDR1 process efficiency is closely linked by the content of metals, organic compounds, activated carbon, and the type of grinding. So, based on each specific material used as input to the process, tests to evaluate the metal extraction yields are always necessary.

Below are some comments regarding the GDR2 recycling process for some specific components of the board:

a. There are different components in each dashboard with various content of base metals and precious metals. These components underwent chemical dissolution in two stages of leaching, according to GDR2 process. The results showed that in some cases metal recovery is not satisfying, which needs more investigation in further studies to improve leaching efficiency.

b. Different components in various dashboards are somehow similar and can be categorized as below:
    I. Big Connectors (in black or blue colour)
    II. Display connectors
    III. Small PCB
    IV. Golden wires (small and large)
    V. LCD pins
    VI. CPU

c. Two scenarios can be considered for selective recovery of metals of interest: first with the possibility of recirculation of the solution after metal precipitation, for using in a new leaching, and second, with disposal of final solution in which, final solution is sent to wastewater treatment stage. The relevant flowcharts were presented in the text.

d. Based on lab tests it is estimated more than half of the initial E-waste is remained at the end of leaching as solid residue, which should be treated properly.

e. Selective recovery experiments were performed after leaching stages. In these experiments Au and Ag were recovered by adding ascorbic acid as reducing agent, and decreasing temperature, respectively. Copper and tin were recovered by cementation method using Sn and Zn powder, respectively.

f. Recovery efficiency for different stages of metal precipitation was not satisfying in selective recovery of precious metals, but almost all of Au, Ag and Pd were precipitated in the next cementation steps. So, these selective metal recovery stages need to be modified.

g. Economic calculations showed that the cost of consumed chemicals for treating 1 ton of components in only one cycle of process (without recirculation) is about 2179 €, which can be reduced significantly by recirculating the solution to the new leaching cycles.

Therefore, the next steps are related to the modification and optimization of the leaching stages and selective metal recovery, in order to increase metal recovery and the purity of final products. Another crucial point is the proper management of final solid residue which, as stated, is more than half of the initial E-waste, and the purging a fraction of solution for wastewater treatment in each cycle of the process. Finally, a correct economic calculations and market analysis can be performed, considering these aspects, to propose the suitable size of a potential industrial plant for treating this kind of waste.

Abbreviations

ANOVA	Analysis of variance
CAPEX	Capital Expenditure
GDR1	Gold-REC 1 UNIVAQ patent
GDR2	Gold-REC 2 UNIVAQ patent
MLD	Minimum liquid discharge
OPEX	Operational Expenditure
PCBs	Printed Circuit Boards
SMD	Surface Mounting Device

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TREASURE

D5.4: Pilot-scale reconfiguration, testing and optimization of a materials recovery process

Annex 4 – Recycling process optimization of Indium-Tin Oxide glass from Liquid Crystal Displays

31/05/2023 (M24)

Author: Nicolò Maria Ippolito, Francesco Vegliò, Svetlana Zueva (UNIVAQ)

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TABLE OF CONTENTS

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1. State of the art/background

Liquid crystal displays (LCDs) are waste electronic and electric equipment (WEEE) that contain a wide range of compounds, some toxic or hazardous. In contrast, others like base and precious metals are valuable and can be recovered. Many European policies pointed out the recovery of scarce resources like critical raw materials (CRMs).

Waste LCD panels are generally disposed of in a landfill or by incineration. However, not only do their disposal through such inadequate approaches result in the wastage of resources, but may also adversely impact the environment and human health; owing to the hazardous nature of some of the panel components.

LCD panels consist of LCs (Liquid Crystals), indium, glasses and other rare metals and organic materials. LCs is stable, non-degenerate and have high unit price. Indium is rare in Earth's crust. Glasses are a kind of alkaline earth boro-aluminosilicate with high purity and stable compositions. These three materials have higher recycling values than other materials in LCD panels. Therefore, efficient recycling of the materials from waste LCD panels and their further reuse can generate economic benefits while contributing to environmental preservation.

Typical LCD has a complex structure Typical composition of an LCD are shown in the Figure 1.

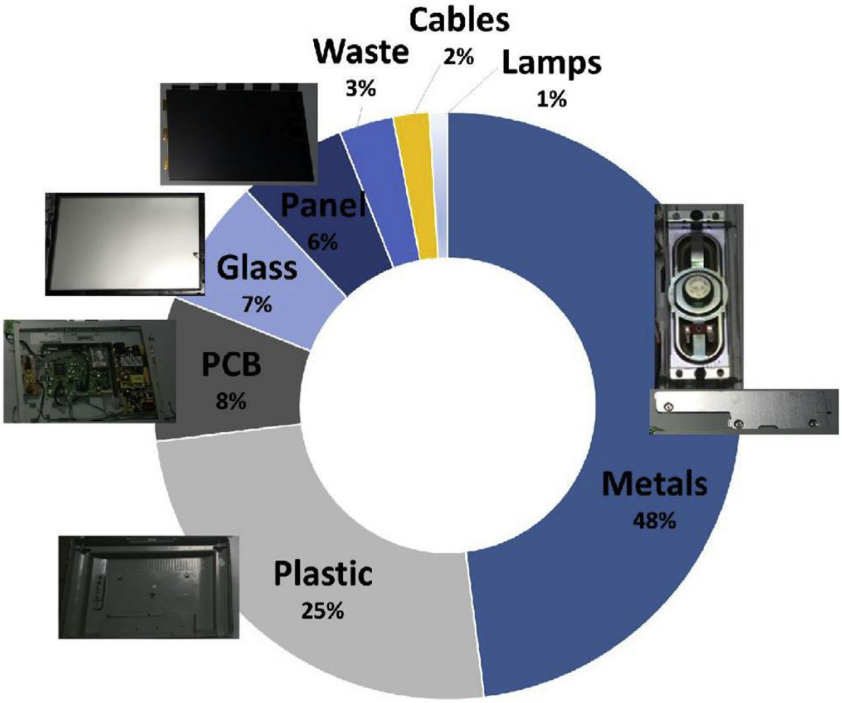


Figure 1. Average composition of an LCD (adapted from Amato et al., 2017).

An extensive study on how to enhance the resource efficiency of energy using products, with a special focus to LCDs, was carried out by **Ardente and Mathieux (2014)**. The proposed method is divided into five steps: reusability, recyclability, recoverability, recycled and use of hazardous substances. **Peeters et al. (2013)** concluded that recycling of TVs by mechanical treatments achieves recovery of less than 10% of the precious metals, while the manual dismantling of such waste increases the recovery of more than 90% of metals. Regarding printed circuit boards (PCBs), automatic pre-treatments like gravity, magnetic, electrostatic, density and pneumatic separation are usually used to recover metals, but they are characterized by heavy metal loss up to 35% (**Birloaga et al., 2013**). **Ferella et al., (2017)** investigated a full recycling process in order to recover all the valuable fractions from LCD panels. That work started in 2009 in the ambit of the 7th FP of the European Union (ID FP7-SME-2008-1 HydroWEEE (2009–2012) and continuing within the second HydroWEEE-DEMO 308549 project (2012–2016).

Almost 98% of an LCD monitor can be recycled. All plastics are removed to be recycled into new products. Printed circuit boards can be recovered from LCD recycling and smelted to recover valuable metals, while cabling is stripped to reclaim copper and other metals.

Waste LCD panels recycling process can transform the panels' material (liquid crystals, indium, and glass) into valuable, reusable products, not only increasing profits but effectively reducing the production of waste material. Recycling of glass from dismantled LCD panels can be carried out directly, for instance as raw material for production of glass-ceramic tiles (**Kim et al., 2016**). Indeed, the most recent studies report processes for valuable component and metal recovery from LCD, using the approach of urban mining in which the waste becomes a source of secondary raw materials. An important task is to develop a full recycling process in order to recover all the valuable fractions from LCD waste.

1.1. ITO glass recycling

Currently, more than 55% of global indium production is consumed for indium tin oxide (ITO) production because of its excellent display properties mainly driven by demand for flat panel displays (FPDs) or LCDs (**Park et al., 2023**). At the end of life, the waste LCD flows to the e-waste stream, accounts for 12.5% of the global e-waste, and is forecasted to be increasing progressively. These waste LCDs are potential wealth for indium that poses a threat to the environment.

Particular interest is recycling ITO glass (Indium Tin Oxide coated glasses) with In recovery. ITO glass (Figure 2) allows the surface to be electrically conductive and utilized in many industries and with multiple applications, from the display, medical devices, and instruments to space exploration. The most common use is for touchscreen devices, from standard cellphones to large-screen retail displays. Indium tin oxide is typically encountered as an oxygen-saturated composition with a formulation of 74% In, 18% Sn, and 8% O by weight.

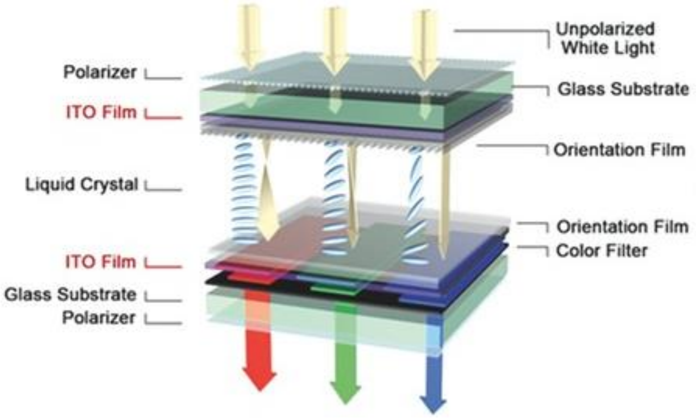


Figure 2. Standard LC device (adapted from Guo et al., 2017)

As it can be seen from the Figure 3, in 2022, China was the world's largest refinery producer of the soft metal indium, having produced 530 metric tons. Global indium refinery production amounted to 900 metric tons that year (Statista, online website).

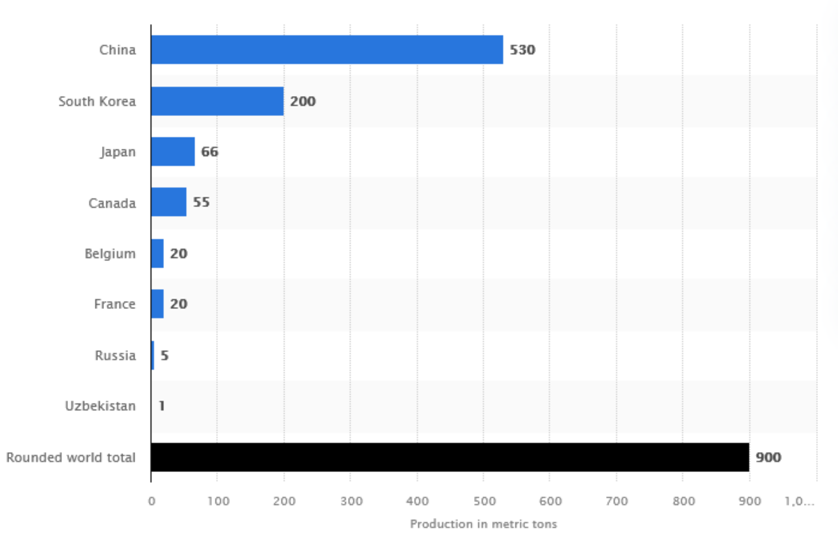


Figure 3. Production volume of indium worldwide in 2022, by country

Indium is one of the strategically important materials that have been characterized as critical by several industrialized countries. Up until 2025, the yearly demand for this material is estimated to grow by 70% relative to the year 2015. In 2011, 1220 t indium was primarily mined worldwide, from which 660 t indium was refined. Over 55% of the worldwide production of indium is used in the ITO (indium tin oxide) target industry, which is a major component in the production of liquid crystal displays (LCD) (Figure 4).

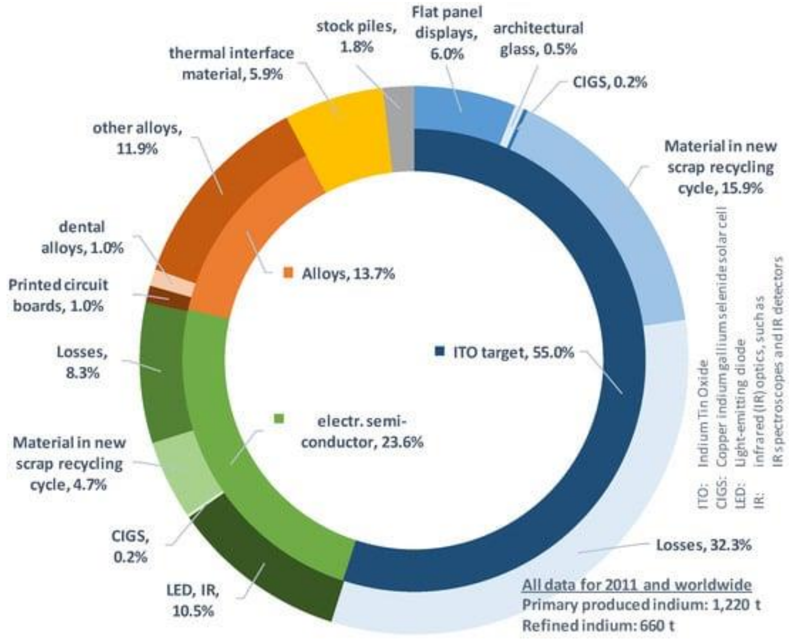


Figure 4. Overview of the application of refined indium worldwide in 2011 (adapted from Licht et al., 2015)

Indium has a sustainability index equal to 0.82, whereas the end-of-life recycling input rate is 0% (**Ferella et al., 2017**). The sustainability index is a measure of the difficulty in substituting the material, scored and weighted across all applications. Values are between 0 and 1, with 1 being the least substitutable. The recycling input, instead, take into account the proportion of metal and metal products that are produced from end-of-life scrap and other metalbearing low grade residues in end-of-life scrap worldwide. As previously mentioned, indium plays a crucial role in our electronic devices, so that it is important to develop and improve new recycling methods. In this perspective, it would be very interesting to estimate the impact of recycled indium that could be reasonably recovered from WEEE.

The main steps in LCD recycling process according to **Amato and Beolchini (2018)**, are:

1. Pre-treatment for disassembling
2. Glass recovery
3. Indium extraction and recovery
4. Integrated recovery of materials (the liquid crystal, the polarizing film and the glass cullet)

LCDs contain two glass plates sandwiching a liquid-crystal mixture. The outer plate surfaces covered with polarizer films, but the inner plate surfaces contain a functional indium tin oxide film. Indium is a critical raw material with limited supplies and high costs. Several possible recycling methods have been developed in recent years. One of possible recycling process line for LCD panels is shown in the Figure 6. It demonstrates the possibility of the selective separation of the glass substrate, polarizer foils, and the elements indium and copper into an individual output.

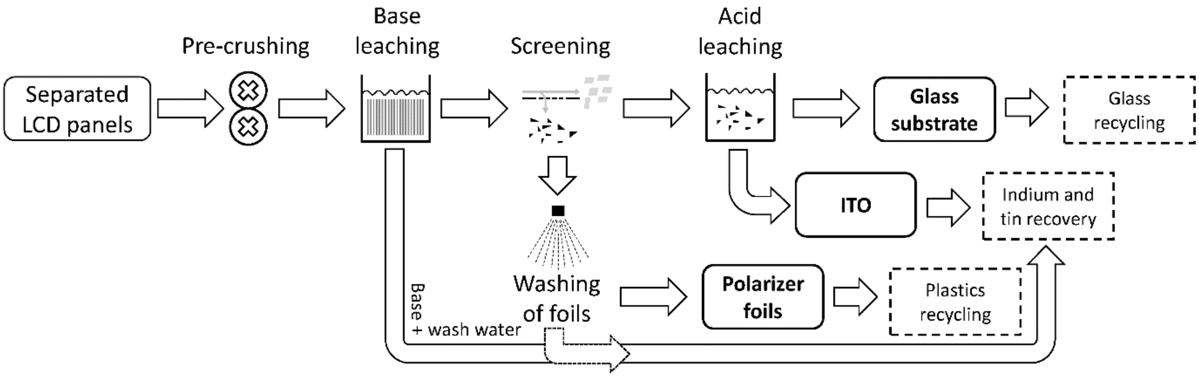


Figure 6. Recommended processing of LCD panels from screen devices for the recovery of indium, tin, glass substrate, and plastics (adopted from Ueberschaar et al., 2017)

Ueberschaar et al. (2017) developed recycling approach based on a composite separation test (CST) and dissolution of the ITO from the glass substrate conducted on samples taken from smartphones and tablets. The mass flow analysis was carried out, depicted on a material level in a percentage and on an element level as mg/kg input material in order to assess the quality of the generated output fractions. Figure 5 shows the results.

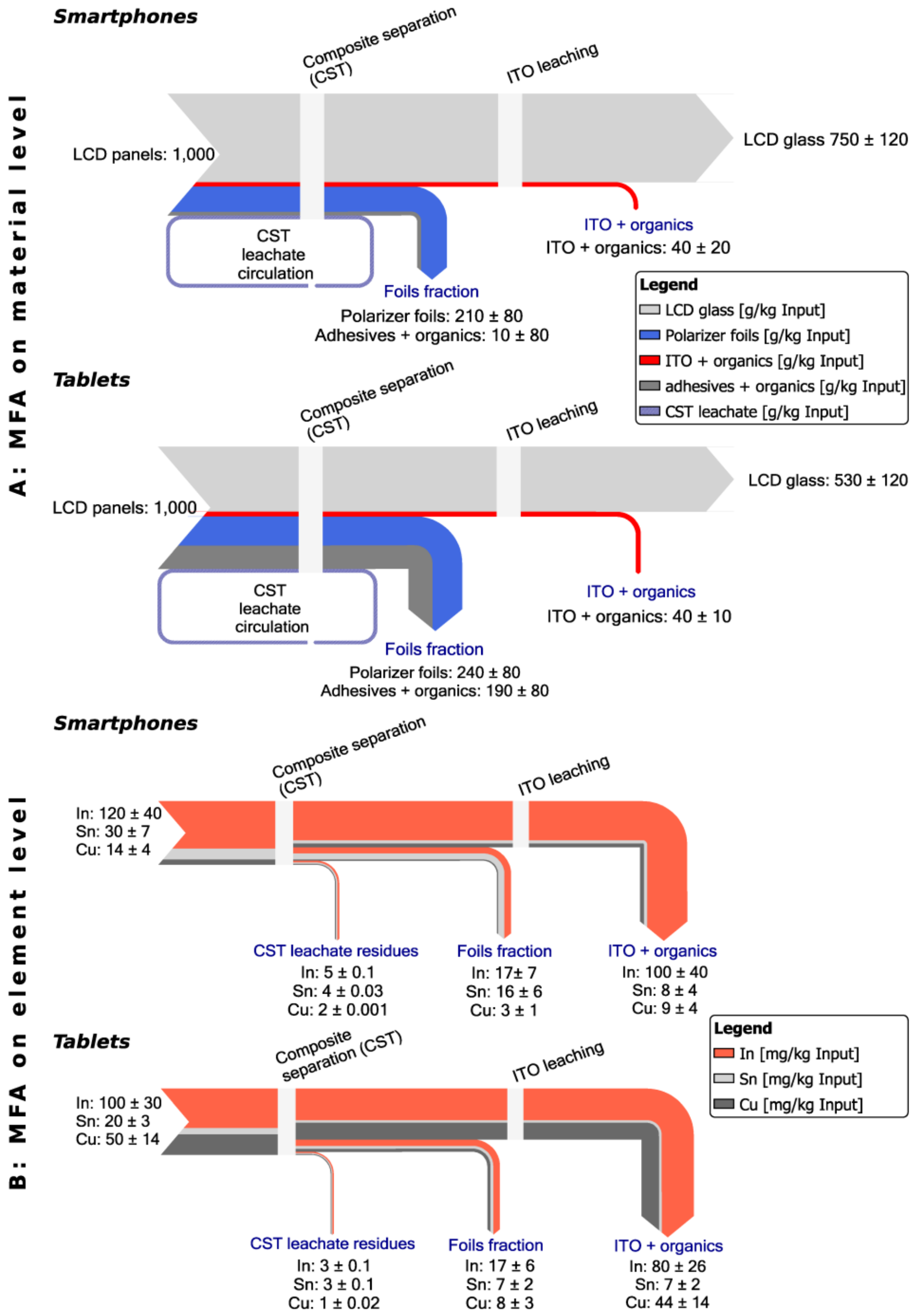


Figure 5. Mass flow on a material and on an element level of a composite separation test (CST) carried out with samples from smartphones and tablets: (A) material level (top) and (B) element level (below). All data normalized to 1000 g input material (adopted from Ueberschaar et al., 2017)

The most common approach for indium extraction is the leaching by strong either acid or base solutions, followed by the recovery, carried out through different approaches. In this regard, the patent CN105063364 includes a first high pressure washing, followed by a metal concentration by roasting, a leaching, an extraction and a final indium replacement by aluminum, obtaining an overall recovery efficiency higher than 90% **(Fan et al., 2015a; Guan et al., 2015; Homma et al., 2011; Muratani et al., 2010; Son and Choi, 2013; Toro et al., 2012; Yano et al., 2005)**. An alternative recovery approach is proposed in patent US2010101367, in which particles of a metal having a larger ionization tendency than indium, are fluidized into the leaching solution, promoting the indium precipitation on the metal particles surface, with a yield greater than 80% **(Muratani et al., 2010)**.

Hydrofluoric acid solution is used as indium high solubility leaching agent in patent US2011017020, that treats several kinds of end-of-life equipment (including LCD) and chooses the electrolysis as the recovery method for: indium, zinc, yttrium, europium, lanthanum, terbium, gadolinium, antimony, lead, copper, tin, and silver (**Homma et al., 2011**).

As an alternative, hydrochloric acid is selected as high-performance extracting agent in patents CN204779739 and JP2005334838. In the first case, the acid is added to a fixed bed pyrolysis oven for the production of indium chloride to collect on a silica wool entrapment (**Guan et al., 2015**).

The sulfuric acid is used in the inventions CN103602815 and RS20100480, different for the specific applied conditions. Indeed, the first one describes a more complex treatment, where an ultrasonic leaching is followed by a high purity indium extraction/back extraction and a final metal replacing, at different pH conditions (**Son and Choi, 2013**).

On the other hand, the presence of hydrogen peroxide, as oxidizing agent, which reduces the liquid crystal foam, characterizes the leaching of the second patent, that shows a final indium recovery by zinc cementation (**Toro et al., 2012**). A completely different approach is used in patent CN104911360 that involves a thermal treatment (at around 400-500 °C for 20-40 min) with the addition of PVC (polyvinyl chloride) powder to produce volatilized indium chloride.

At low-pH conditions Indium exist mainly as dissolved free indium ion, In^{3+} (**Wood and Samson, 2006**), although some fraction of this could be colloidal:

$$\mathrm{In(OH)_3}(s) = \mathrm{In}^{3+} + 3\mathrm{OH}^-; \mathrm{K}_{sp} = \{\mathrm{In}^{3+}\}\{\mathrm{OH}^-\}^3$$

$$\mathrm{In}^{3+} + 3H_2O = \mathrm{In(OH)_3(s)} + 3H^+; \mathrm{K}_f = \{\mathrm{H}^+\}^3/\{\mathrm{In}^{3+}\}$$

At low pH (<3), indium is completely dissolved (i.e. passes through a 0.45 µm filter), instead at pH>8, indium associates with suspended solid phase (Figure 6 and 7).

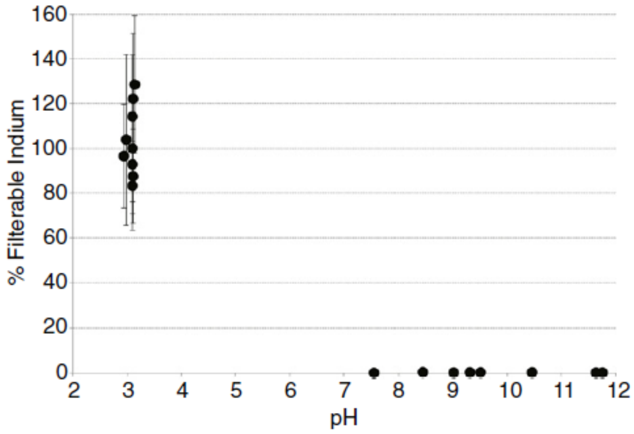
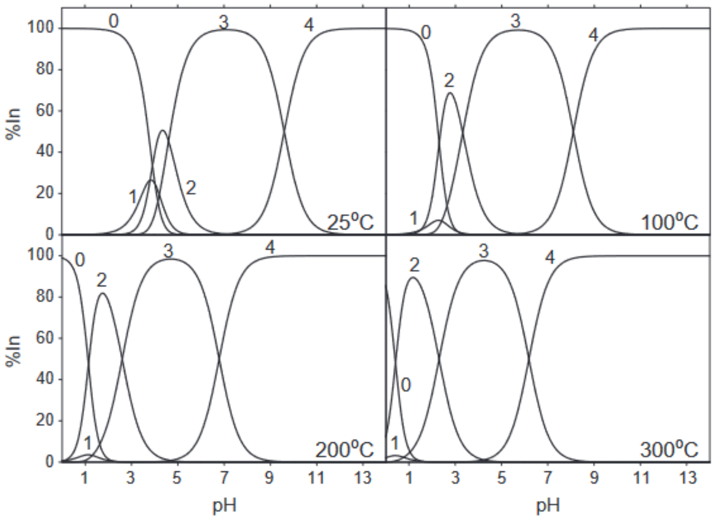


Figure 6. Filterable indium as a function of pH (adopted from Wood and Samson, 2006)



Distribution of mononuclear In–hydroxide species as a function of temperature and pH at SWVP and infinite dilution. The species shown are: 0—In^{3+}; 1—$InOH^{2+}$; 2—$In(OH)_2^+$; 3—$In(OH)_3^0$; and 4—$In(OH)_4^-$.

Figure 7. The aqueous geochemistry of indium (adopted from Wood and Samson, 2006)

Jiang et al. (2011) proposed indium enrichment process by the precipitation method using sodium tripolyphosphate (Na5P3O10). Indium after precipitation was further separated and purified by solvent extraction. The indium precipitation percentage was above 95% when the pH value was 2.6, the reaction time was 1.5 h and the molar ratio of sodiumtripolyphosphate to indium was 0.91. The precipitate was dissolved with NaOH solution. Then the hydroxide obtained was leached with sulfuric acid solution. The solution obtained from the leaching of the precipitate was much more appropriate for solvent extraction process.

Yoshida et al. (2015) did report that 83% indium was recovered from CF glass and 10% from TFT glass of LCD panel wastes using sub-critical water at 360 ◦C.

Argenta et al. (2017) demonstrated an effective method for indium extraction from liquid crystal displays (LCD) screens of cell phones using alternative organic acids. Leaching tests were performed with supercritical CO_2 and co-solvents, as well as under conventional conditions using citric and malic acids. Results showed that at atmospheric pressure, 76.5% of indium was extracted after 180 min. The use of supercritical CO_2 besides providing a reduction in extraction time also provides a higher extraction, reaching 94.6% in just 30 min.

Recently, solvent extraction of Indium(III) by different kinds of extracting agents has been reported mainly **(Alguacil, 1999; Lee et al., 2002; Liu et al., 2006; Gao et al., 2010)**. **Kato et al., (2013)** proposed separation and concentration of indium from a liquid crystal display (LCD) by homogeneous liquid–liquid extraction (HoLLE). More than 96.7% of the indium was extracted from the simulated leaching solution into the sedimented liquid phase.

The selective recovery of indium from spent LCD leachates by ion exchange very promising technique. **Fortin-Lecomte et al. (2022)** demonstrated the ability of the Lewatit VP OC 1026 resin, to efficiently and selectively sorb indium selectively from mixtures with other impurities. The elution of In(III) can was achieved with a 1 M HCl solution. A final concentrated solution was obtained at the end of the fixation/elution tests.

Assefi et al. (2018) did study three macro porous styrene-divinylbenzene resins (Lewatit TP 208, Lewatit TP 260 and Amberlite IRA 743) for solid-liquid recovery of In(III) from LCD scraps. Firstly, the process was carried out by milling of LCD panel, then leaching and followed by adsorption/desorption of In(III). Adsorption of the In(III) was optimized at pH of 2, 0.5 g resin loading, temperature of 25 °C for 30 min. Symmetrical molecular form of functional group (iminodiacetic) on the surface of the Lewatit TP 208 adsorbed In(III) more efficient than two other resins and is a promising ion exchange resin for recovery of indium from scrap LCD panels.

Indium recovery via electrowinning from nitric and very extensively chloride electrolytes combined with stabilizing compounds was subject of many studies **(Lee et al., 2004; Chou et al., 2009; Wu et al., 2017)**. Although using these two acid electrolytes in electrowinning is possible to obtain uniform deposits and low specific energy consumption (SEC), environmental issues endanger the technical and economic process stability. The dangers of chlorine gas require a sealed and expensive system, to avoid dangers for human health. Therefore, different electrolytes with no pollutant and toxic gases emissions and less powerful corrosion effects are proposed as a suitable measure to perform more affordable indium electrowinning.
Ciro et al. (2020) did investigate indium electrowinning process using a sulfate electrolyte on stainless steel, nickel, titanium, aluminium and copper cathodes. Based on the results obtained, a real influence of the material cathode on indium electrowinning processes has been observed. It was concluded that nickel and stainless steel (SS) were the most suitable cathodic supports for indium electrowinning from sulfate solution. Indium was deposited using a current density of 25 A/m^2 for 22 h at 40 °C and pH 2.3.

1.2. PCB recycling

PCB recycling begins with the physical process of drilling/sorting the boards to remove components, and then cutting the boards into smaller chunks. This process removes capacitors, motors, batteries, plugs, semiconductors, LEDs, fasteners, and other parts from a PCB. Additionally, magnetic separators pull ferromagnetic materials away from non-ferrous metals and any non-magnetic waste. The Waste Electrical and Electronic Equipment Directive (WEEE Directive) and the Restriction of Hazardous Substances Directive (RoHS) require different recycling methods for those components.

After cutting and sorting PCB boards, most firms rely on either pyrometallurgy, hydrometallurgy, or electrochemical processes to break down the boards and retrieve precious materials. The pyrometallurgical process includes heating the PCB to a high temperature in order to recover the material. Hydrometallurgical processes utilize aqueous leaching agents consisting of nitric acid, sulfuric acid, and aqua regia to recover metals.

PCBs have a ratio consisting of 40% metals, 30% organic materials, and 30% ceramics. Therefore, recycling processes recover approximately 99% of copper, copper-beryllium alloys, beryllium oxide, aluminium, tin, gold, silver, platinum, palladium, and lead from a PCB board.

2. Materials and methods

2.1 Chemicals and Solutions

All chemicals were used as received and without any further purification: HCl 37% w/w, HNO_3 65% w/w, H_2SO_4 96% w/w, $FeSO_47H_2O$, H_2O_2 30% v/v. Hydrated lime ($Ca(OH)_2$) 20 % (w/v) and NaOH 1M were used as the reagents in precipitation tests

The ion exchange resins (Amberlit® IRC 748, Lewatit® TP 214, Amberlit® IR 120 and Amberlite® XAD 7HP) were obtained from Sigma-Aldrich.

2.2 Experimental Procedures

2.2.1. Acid attack

The acid attack was performed in a 250 mL closed flask as follows: initial material was submerged in 50 ml solution of 1:3 of nitric acid (VWR Chemical, 65%) and hydrochloric acid (VWR Chemicals, 37%) at 150 ◦C for 3 hours.

2.2.2. Neutral leaching test (washing)

Neutral leaching tests were carried out at room temperature in a jacketed stirred reactor tank at glass/water ratios (1.5:10) by mixing at 100 rpm for 1 h. Afterwards a sample were filtered, and leach liquor was taken to measure the concentration of In, Sn and COD. Instead washed ITO glass was subject of acid leaching.

2.2.3. Leaching test

Leaching tests were performed in 250 mL closed flasks submerged in a thermostatically controlled water bath (at 60°C for 1.5 h) equipped with a mechanical stirrer (Dubnoff, ISCO) (150 rpm).

The experiments were carried out with the goal of defining the effect of time, solid/liquid and sulphuric acid on the maximum effect of In removal from ITO glass.

Before acid leaching step ITO glass samples were washed with distillate water, so called neutral leaching step. Tests were carried out at room temperature S/L ratios 3/10 by mixing at 150 rpm for 1 h. Afterwards liquid phase was separated from washing solution and glass samples was subject of acid leaching. Instead washing water was recycled for other neutral leaching tests.

The chemical leaching tests of the ITO glasses samples were carried out at a lab-scale in an open glass vessel system. Sulfuric acid was used. In order to define the best operative conditions for indium leaching, preliminary tests were performed on ITO glass by varying concentration of leaching agent (0.1, 0.3 and 0.5 M) and the liquid/solid ratio (S/L = 6/10, 3/10 and 1.5/10); The time was 2 hours and the temperature was 60◦C in all the experiments. Subsequently, the glass was filtered by a vacuum pump (Millipore) and the solution was stored for ICP analysis.

Indium leaching efficiency (*E*%) was calculated according to Eq. (1):

$$E = \frac{M}{M_0} 100\% \qquad (1)$$

where *M* is the amount of indium dissolved (g); M_0 is the amount of indium in the initial sample (g).

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The study consisted of three sets of experiments:

1. Neutral leaching
2. Direct leaching
3. Cross-current leaching with acid recycle
4. Counter-current leaching process (CCLP)

To eliminate the effect of sample variability on the results of experiments in leaching tests, In content in the solid residue after leaching and subsequent acid attack was measured.

2.2.4. Indium electrowinning experiments

In order to recover indium from the sulfate electrolyte, an electrowinning process was proposed. In this electrowinning process Cu was used as metal cathodes to carry out indium deposition, while a graphite as an anode. The electrodes (4.5 cm long with diameter 0.7 cm) were then fixed at 4 cm distance for all electrowinning experiments. The reduction process was assisted with a current density (27-28 A/m^2) for 2.5 h at ambient temperature. Electrowinning process was assisted with constant stirring of the electrolyte at 100 rpm to remove the possible hydrogen bubbles formation on the cathodes.

2.2.5. Ion-exchange resins experiments

Masses of 0.5 g (dry basis) of each resin (Amberlit® IRC 748, Lewatit® TP 214, Amberlit® IR 120 and Amberlite® XAD 7HP) were added to 50 mL of leachate and stirred for 2 hours at ambient temperature. The mass of the resin used was selected to ensure that the number of exchange sites present on the resin was greater than those required to fix all the In(III) present in the leachate. Subsequently, the samples were filtered to separate the resins from the leachate. Before use, all ion exchange resins were rinsed three times with distilled water at 150 rpm for 10 min.

The percentage of In(III) adsorbent on the resins (Removal %) were obtained by the Eq. (2)

$$E = \frac{C}{C_0} 100\% \tag{2}$$

where C and C_o are the initial and equilibrium concentration of In(III) in aqueous solution before and after batch sorption, respectively.

2.2.6. In precipitation experiments

Precipitation experiments were carried out in a 100 ml glass beaker with leachate. pH was increased incrementally with the addition of 1M NaOH. Equilibrium pH was then recorded, and the samples were filtered. The In and Sn concentration remaining in solution was analysed.

2.2.7. Experimental Design and Data Analysis

Mathcad Software (version 13.0) was used for data analysis. Central composite design (CCD) was applied to optimize the two most important operating variables: the sulphuric acid concentration and solid part content (for every 100 g of water - 60, 30 and 15 g of glass waste) (Table 1).

Table 1. Factors and levels investigated in leaching tests.

Factor (Variable)	Level		
	-1	0	+1
H_2SO_4, M	0.1	0.3	0.5
Solid content, %	60	30	15

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2.2.8. Wastewater treatment (Advanced oxidation Processes)

Advanced oxidation Processes (AOPs) or Fenton process was performed in order to evaluate the efficiency of physical chemical pretreatment of the Sample 1 washing water. The Fenton reaction is one of the most commonly used AOPs in which $FeSO_4$ (Fe^{2+} ions) act as catalysts, and hydrogen peroxide (H_2O_2) as the oxidizing agent:

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe + HO_2\bullet + H^+ \qquad (2)$$

The traditional dosing mode of the reagents was adopted. The Fenton process was performed with $FeSO_4{\cdot}7H_2O$ as a source of Fe^{3+} under optimal conditions ratio [COD]:[H_2O_2] = 1:9; ratio [H_2O_2]:[Fe^{2+}] = 4.5:1 and pH 3-3.5. Samples of the wastewater were heated up to the desired constant temperature (40◦C). After what $FeSO_4$ was added to the reaction mixture. Finally, Fenton reaction was started with the addition of H_2O_2 (30% w/v). The solutions were stirred (200 rpm) during the reaction period up to 120 min at a temperature of 20 °C.

After reaction were completed, precipitation of the oxidized iron as $Fe(OH)_3$ was performed by adjusting the pH up to 8 by neutralization with NaOH (40% w/v) for 1 h and following filtration.

The wastewater was characterized in terms of pH, TSS and COD content content before and after the Fenton's oxidation experiments.

2.3 Methods of Analysis

An X-ray fluorescence XRF spectrophotometer (Spectro XEPOS 2000) was used to perform the qualitative chemical analyses. X-ray diffraction (XRD, PANalytical X'PertPRO diffractometer) was used to characterize the ITO glass samples.

A quantitative analysis was also carried out by Agilent Technologies 5100 ICP-OES atomic absorption after acid attack in order to evaluate the metals content.

All of pH measurements were performed with a digital pH meter. COD was measured with Dr. Lange's kit, cuvette-test LCK 114A.

Mettler Toledo G20S Compact Potentiometric Titrator was used for sulphuric acid and leaching solution titration.

The total suspended solids (TSS) were measured by Standard Method 2540 for solids determinations within the water and wastewater industry (Clescerl et al., 1998). The solution was filtered with a 0.2 lm syringe filter. Ten mL of the collected clarified filtrate was added to a pre-weighed aluminum weigh pan and the same analysis described above for total solids determination was repeated. Samples were cooled and a final mass of dry total suspended solids was obtained by difference. The initial percentage of water was calculated. Duplicates of all samples were analyzed and reported results represent the average.

3. Characterization

3.1. ITO glass

Processing this waste was studied on two types of ITO glass.

The first ITO glass (Fig. 8(a)) was 0.55mm thick 80 ohm/sq - where ITO layer is 30±5nm thick. It is commonly used in head-up displays and screen types of displays.

The second ITO glass (Fig. 8(b)) was 0.7mm thick 4.5 ohm/sq - where ITO layer is 350±30 nm tick and coated on both sides. This is used in cockpit dot-matrix/alfa-numeric displays where DSTN (double cell super twisted nematic) or heating for low temperatures are used.

The study aimed to work out a detailed analysis of the recycling process for In recovery.

(a) (b)

Figure 8. LCD – ITO GLASS (a): Sample 1 (transparent, 2x3 cm pieces); (b) – Sample 2 (green, 2x2 cm pieces)

The sample was attacked by aqua regia, and the resulting solution was subsequently analyzed by ICP-OES to determine the In and Sn content. The study of these two metals was dictated by literature analyses and by economic/critical interest (Amato and Beolchini, 2018).

Table 2 summarizes the average composition of ITO glasses in terms Indium and Tin.

Table 2. Chemical composition of ITO glasses (ICP-OES analysis).

Chemical attack	In [kg/t]		Sn [kg/t]		Average	
	min	max	min	max	In, %	Sn, %
Sample 1	0.060	0.070	0.015	0.020	0.007	0.002
Sample 2	0.925	1.890	0.129	0.243	0.12	0.01

The chemical composition was also defined by performing XRF analysis. The main components are shown in the Table 3. In addition to indium and tin were found only elements due to the glass. The other detected elements have a concentration below 1 %.

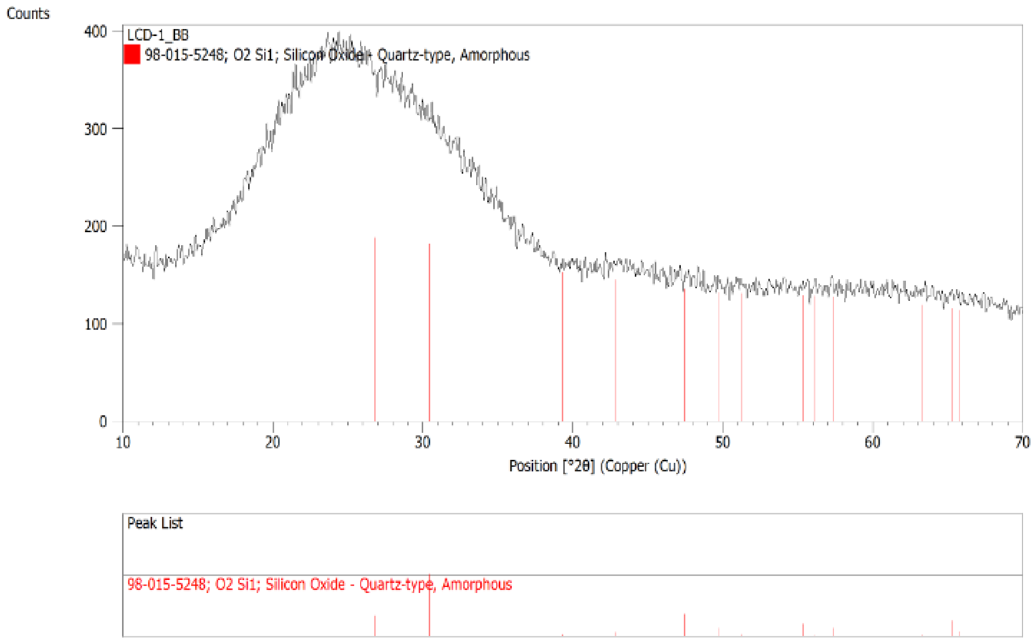
Table 3. Chemical composition of ITO glass (XRF analysis)

Elements	Sample 1	Sample 2
Si, %	37.9	30.5
Mg, %	4.4	2.7

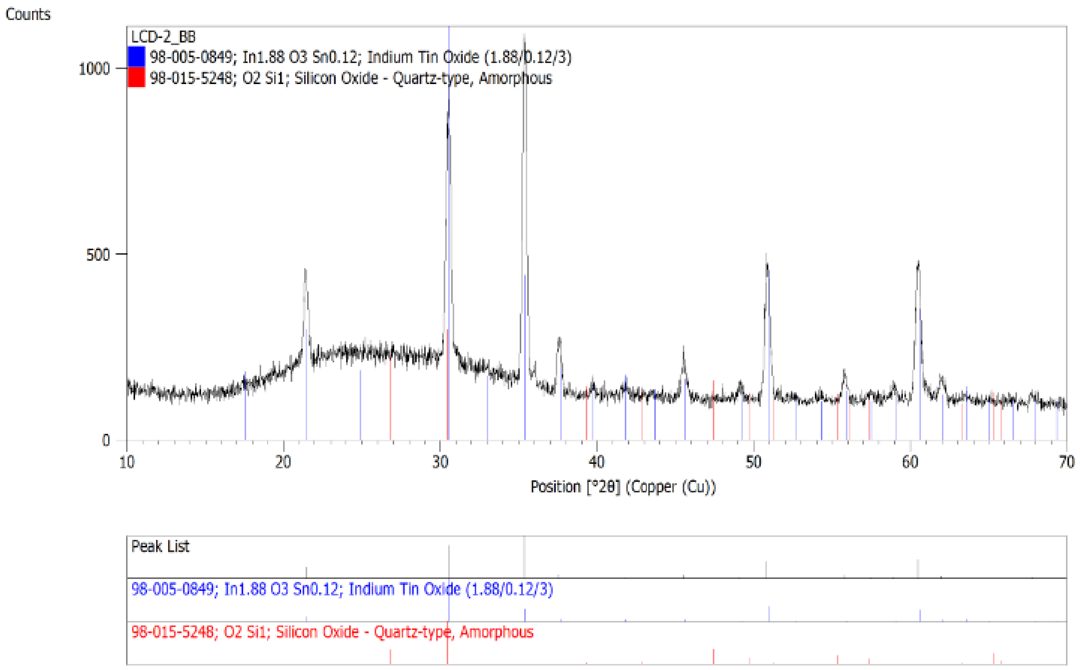
Ca, %	4.8	5.4
S, %	1.6	0.1
K, %	<1	1.5

The XRD pattern (Figure 9) shows characteristic Bragg peaks:

- Sample 1, ITO layer is 30±5nm thick - because of the low concentration of In (0.071 kg/t) and Sn, only the hump related to the presence of an amorphous phase (glass) is evident.
- Sample 2, ITO layer is 350±30nm thick - in this case, the highest concentration of In (1.186 kg/t) and Sn allows identifying indium-tin-oxide peaks.



(a)



(b)

Figure 9. ITO glass XRD patterns: (a) – Sample 1; (b) – Sample 2

4. Recycling process optimization – ITO glass

4.1. Leaching

4.1.1 Neutral leaching

In order to prepare a sample for recovery of indium, all samples of ITO glass were washed with distillate water (15 % of solid: for 15 kg of glass waste - 100 kg of water), so called neutral leaching (Figure 9).

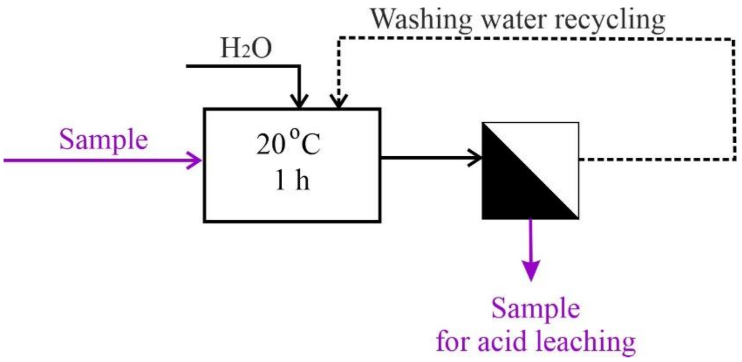


Figure 9. Neutral leaching

Sample 1 washing water right after first step of neutral leaching was rather turbid, it contained dispersed particles. To understand nature of this suspended substance TSS (Total Suspended Solids) and COD (Chemical Oxygen Demand) analysis was performed.

COD is the amount of dissolved oxygen that must be present in water to oxidize chemical organic materials.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101003587

Chemical composition of washing water after neutral leaching without washing water recycling (1 step) and neutral leaching with 3 times washing water recycling (3 step) are presented in the Table 4.

High levels of COD in Sample 1 washing water indicate high concentrations of organics that can deplete dissolved oxygen, leading to negative environmental and regulatory consequences. IT can be assumed that presents of organic substances in spent washing water result from extraction of liquid crystals. The specific compounds of the liquid crystals were not identified.

Table 4. Chemical composition of washing water

	Sample 1 transparent		Sample 2 green	
	1 step	3 steps	1 step	3 steps
pH	2.8	2.6	6.1	6.2
In, mg/L	0.6	1.9	0.07	0.18
Sn, mg/L	0	0	0	0
COD, mg/L	1000	1650	30	70
TSS, mg/L	170	465	<10	<10

Thus, it can be suggested from Table 4 that in case of ITO green glass it is not necessary to add preliminary neutral leaching step. Instead, in case of transparent ITO glass neutral leaching is essential pretreatment process.

The material balance for 1 cycle neutral leaching is given in the Table 5.

Table 5. Mass balance for the neutral leaching

INPUT		OUTPUT	
Description	kg	**Description**	kg
I cycle			
Solid (ITO glass)	1000.0	Solid (ITO glass)	995.0
Water	6666.0	Water	6671.0
Total	**7666.0**		**7666.0**
V cycle			
Solid (ITO glass)	1000.0	Solid (ITO glass)	995.0
Water	1333.2	Water	1338.0
Total	**2333.2**		**2333.0**

Spent neutral leaching solution after Sample 1 washing can be recycled maximum 3 times after what has to be treated by Fenton process with further neutralization and filtration.

4.1.2 Direct leaching

Previous study (Treasure D5.3) of Sample 1 (transparent glass) leaching, demonstrated maximum indium dissolution yield, at 60 °C; H_2SO_4 concentration 1 mol/L and Solid/Liquid ratio 1.5 (15% wt/v) with a dissolution yield of 99.29 % for indium. In order to further reducing of reagents consumption other tests with a sulfuric acid concentration of 0.5 mol/L were carried out. The dissolution yields were found to be very similar to the best run ones, so the perfect choice is to work with a sulfuric acid concentration.

In order to reduce reagent consumption (water and sulfuric acid) and keep high indium output farther experiment were carry out with help of Central Composite Design (CCD) plan.

All ITO glass sample before leaching were subject to neutral leaching.

In this case object of study was Sample 2 (green ITO glass), rich of In. Previous experiments highlighted that acid concentration and S/L ratio could impact efficiency in a negative manner. Therefore, in order to achieve optimum parameters CCD was applied on two factors: the sulfuric acid concentration and the Solid/Liquid ratio (Table 1) for leaching tests for 1.5 hour at 60°C. Results of experiments and response surface-plot are given in Table 6 and Figure 9.

Table 6. Experimental conditions and results of CCD (Sample 2)

No	Factors		pH	Leaching			Chemical attack			In dissolution, %
	H_2SO_4, M	S/L, %		In mg/L	Sn mg/L	V, ml	In mg/L	Sn mg/L	V, ml	
1	0.1	15	1.2	58.5	2.7	50	50.2	6.9	100	40
2	0.1	30	1.2	123.9	3.4	50	89.3	13.7	100	37
3	0.1	60	1.2	229.1	3.5	50	385.2	73.7	50	36
4	0.3	15	0.9	147.6	10.4	50	17.5	2.4	100	81
5	0.3	30	0.9	180.3	14.6	50	61.3	7.8	50	75
6	0.3	60	0.9	462.1	24.3	50	124.4	19.3	100	65
7	**0.5**	**15**	**0.7**	**84.7**	**11.6**	**200**	**19.5**	**16.1**	**100**	**89**
8	0.5	30	0.7	159.2	29.5	100	225	29.5	50	60
9	0.5	60	0.7	317.5	42.6	50	302	42.6	50	52

CCD identified maximum effect of In dissolution was achieved in case of leaching 0.5 M sulfuric acid with 1.5/10 Solid/Liquid ratio (15% wt/v). Considering that according to previous results, in case of 1 mol/L sulfuric acid and Solid/Liquid ratio 1.5/10 with In dissolution yield was 99.29 %, it may be concluded that 2 times reduction in acid consumption led to a decrease in the yield of indium by only 10%. Instead, in case of 0.1M sulfuric acid there is significant decreasing in In dissolution (from 89% up to 40%) (Figure 10).

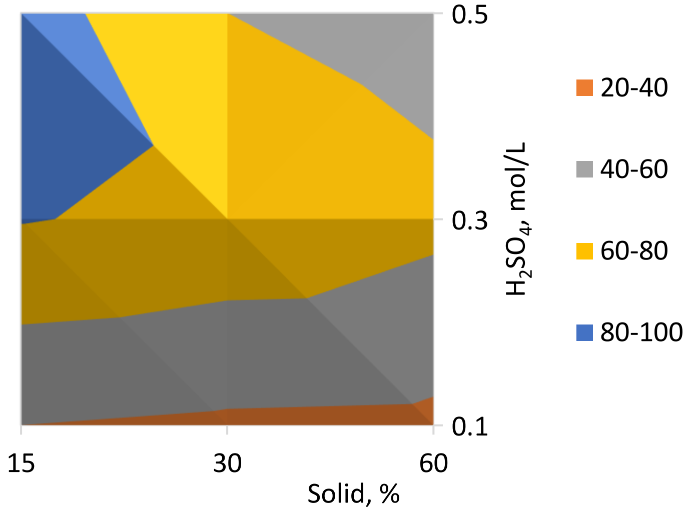


Figure 9. Response plot for indium dissolution yield (Sample 2)

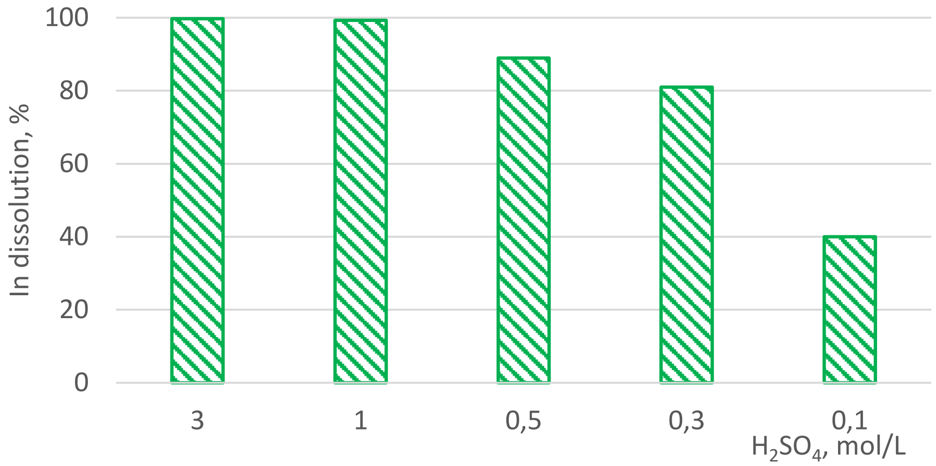


Figure 10. Indium dissolution yield depending on H2SO4 concentration (Sample 2)

Summarizing the following conclusions were made:

a. The optimal ratio of solid and liquid fraction 1.5/10 (15% wt/v)

b. The optimal concentration of sulphuric acid is 1M, however, given that 2 times decrease in sulfuric acid consumption (0.5M instead of 1M) reduces the degree of dissolution of indium by only 10%, 0.5M sulphuric acid can be recommended.

c. It should be noted that pH of In containing solution after leaching with 0.5, 0.3 and 0.1M H_2SO_4 acid are 0.7, 0.9 and 1.2 respectively. This fact can play an important role in choosing the method for indium recovery from leaching solutions.

d. Due to the relatively low concentration of indium in the solution after leaching of 15% wt/v ITO glass, further experiments were carried out on studying cross-leaching process with sulphuric acid recycling in order to reduce acid consumption and increase In content in the resulting solution from one hand. From other hand to obtain solution with higher pH value, that can play important role for In recovery process.

4.1.3 Cross-leaching process (Leach liquor recycling)

Cross flow solid-liquid leaching is a relatively simple unit operation. “Cross flow” means that the solid to be extracted, will be mixed with fresh solvent, drained, mixed with “fresh” acid.

In our case, the main goal was organising of cross-leaching process with sulphuric acid recycling in order to obtain a more concentrated indium solution at the output.

All ITO glass sample before leaching were subject to neutral leaching. 0.5M sulfuric acid was used for leaching experiments.

The cross-leaching method was applied by reusing of spent leaching solution and immersing fresh ITO glass for each other experiment (Figure 11).

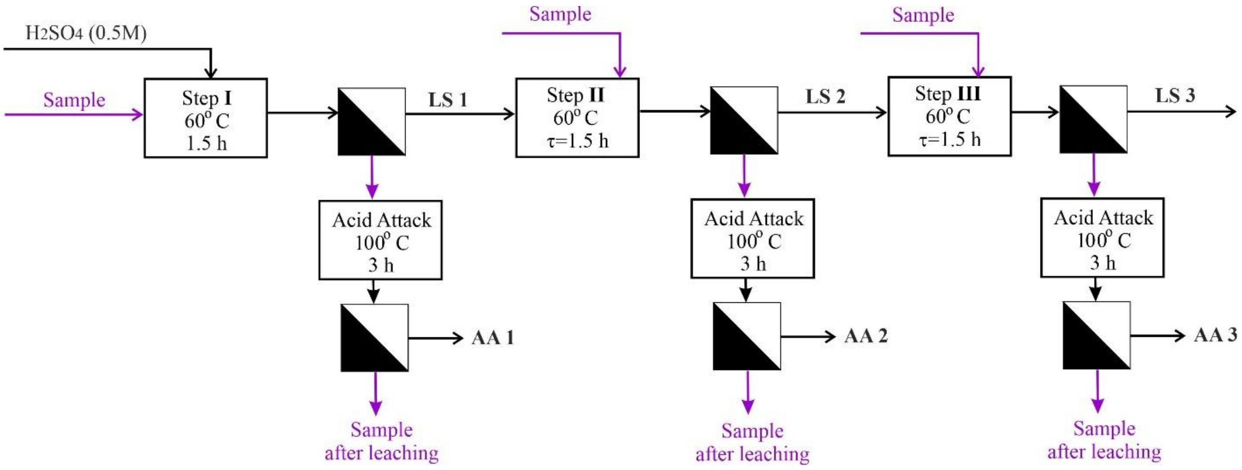


Figure 11. Three step cross-leaching process with acid recycling

As it can be seen from the Table 7, this procedure has lead to the doubling and, respectively, tripling, of indium concentrations into solution. Apart of this, three step cross current leaching with leaching solution recycling can result in 3-time reduction of sulphuric acid consumption.

Table 7. Three step cross-leaching with acid recycle

Step	Leaching (LS)			Acid Attack (AA)			Resa In, %
	In, mg/L	Sn, mg/L	V, ml	In, mg/L	Sn, mg/L	V, ml	
Sample 1							
I	9.2	3.2	200	7.2	4.2	50	83.7
II	15.8	3.5	199	6.4	6.4	50	80.4
III	22.1	4.6	195	19.9	5.5	50	53.8
Sample 2							
I	142.2	11.6	200	115.5	16.1	50	83
II	274.9	13.9	190	97.2	21.2	50	83
III	449.6	25.7	182	53.3	13.5	50	69

As can be seen from the experimental results, Sample 1 contains about 15 times less indium, and as a result of three-step leaching with concentration of the solution, the maximum content of indium was 22 mg/l. Whereas, under the same conditions, leaching of Sample 2 yielded a solution with 450 mg/l indium.

Flow chart of Sample 2 cross leaching process (CLP) with acid recycling is shown in the Figure 12 and the material balance are given in the Table 8.

Table 8. Mass balance for I cycle of the three steps CLP with acid recycle (0.5M H_2SO_4)

INPUT		OUTPUT	
Description	kg	**Description**	kg
Solid (ITO glass)	1000.0	Solid (ITO glass)	974.0
H_2SO_4, 96%	114.6	Leaching solution for In recovery	2248.0
Water	2107.4		
Total	**3222.0**	**Total**	**3222.0**

Summarizing the following conclusions were made:

1. Cross leaching process with acid recycling reduce the consumption of sulfuric acid by three times and increase the content of indium in the leaching solution by 2.4 times for Sample 1 and by 3.1 times for Sample 2.
2. It is not recommended to do more than 3 leaching steps due to a decrease in the yield of indium (1st and 2nd step about 80% third step maximum 60%).

In order to increase the yield of indium and reduce the consumption of sulfuric acid, further counter-current leaching was studied.

4.1.4 Counter-current leaching process (CCLP)

A process flow diagram for counter-current three stage leaching process is shown in Figure 12. The stages are numbered in the direction of the solid (ITO glass) stream. The liquid phase (H_2SO_4 acid) is the overflows continuously from stage-to-stage counter-current to the solid phase, dissolving solute as it moves along.

As it can be seen from the results of experiment three step counter-current leaching results (Table 9) in 99.8% yield of indium in case of 0.5M H_2SO_4 and 99.8% in case of 0.1M. It is mean that organizing process in counter-current manner it is possible almost completely extract In from ITO glass and in the same time 5 times reduce sulfuric acid consume (from 0.5M to 0.1M).

From other hand, after two step CCLP in case of 0.5M H_2SO_4 98% of indium was dissolved, while in case of 0.1M only 78% (Figure 13). Material balance are given in the Table 10 and 11.

Table 9. Counter-current leaching process (CCLP) efficiency.

H_2SO_4	Solid content, % wt/v	Leaching				CCLP 1				CCLP 2			
		In, ppm 1st step	In, ppm 2nd step	In, ppm 3rd step	Yield, %	In, ppm 1st step	In, ppm 2nd step	In, ppm 3rd step	Yield, %	In, ppm 1st step	In, ppm 2nd step	In, ppm 3rd step	Yield, %
Sample 1													
0.1 M	15	2.05	0.8	0.5	**99.7**	6.9	0.5	0.3	**98.5**	4.1	0.4	0.2	**97.0**
0.5 M	15	2.54	0.9	0.4	**99.8**	7.4	0.7	0.1	**99.5**	4.5	0.5	0.05	**99.2**
Sample 2													
0.1 M	15	92.4	67.3	36.2	**99.9**	211.4	56.8	59.8	**99.8**	157.2	54.3	55.8	**99.8**
0.5 M	15	84.7	71.5	12.1	**99.8**	168.7	64.8	3.2	**99.9**	157.8	57.1	2.6	**99.9**

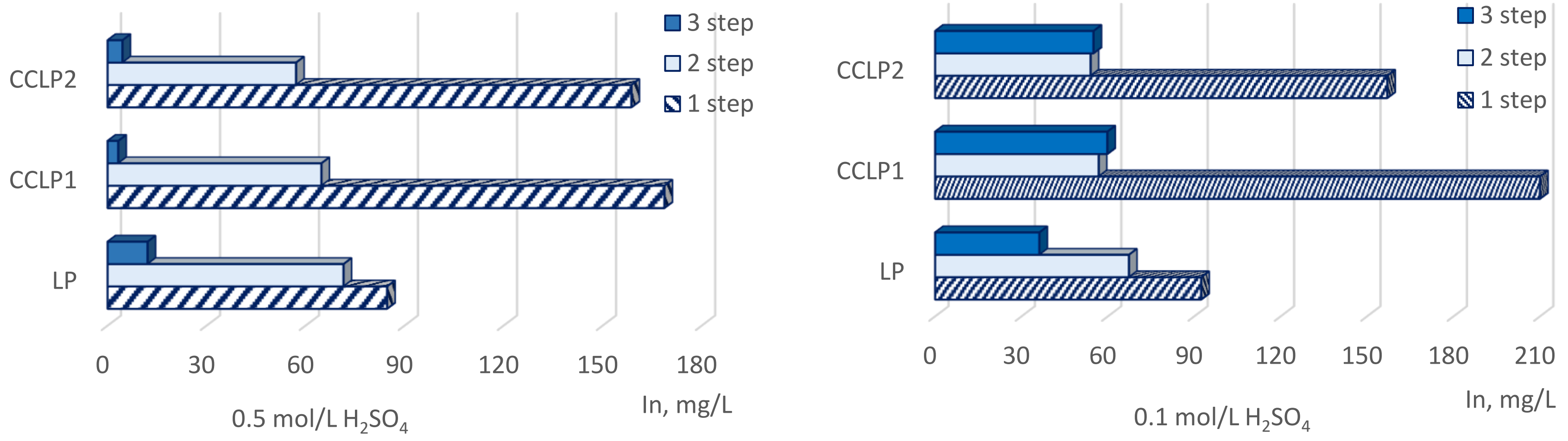


Figure 13. Indium dissolution in three steps counter-current leaching process (1.5h, T = 60 °C) for 0.5 and 0.1M sulfuric acid

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Table 10. Mass balance for regime two step CCLP (0.5M H_2SO_4)

INPUT		OUTPUT	
Description	kg	**Description**	kg
Solid (ITO glass)	1000	Solid (ITO glass)	0.975
H_2SO_4, 96%	343.8	Leaching solution for In recovery	6.691
Water	6322.2	Recycled leaching solution	6.666
Recycled leaching solution	6666		
Total	14.332		14.332

Table 11. Mass balance for regime three step CCLP (0.1M H_2SO_4)

INPUT		OUTPUT	
Description	kg	**Description**	kg
Solid (ITO glass)	1000.0	Solid (ITO glass)	981.0
H_2SO_4, 96%	68.7	Leaching solution for In recovery	6685.0
Water	6597.3		
Recycled leaching solution	13333.0	Recycled leaching solution	13333.0
Total	20999.0		20999.0

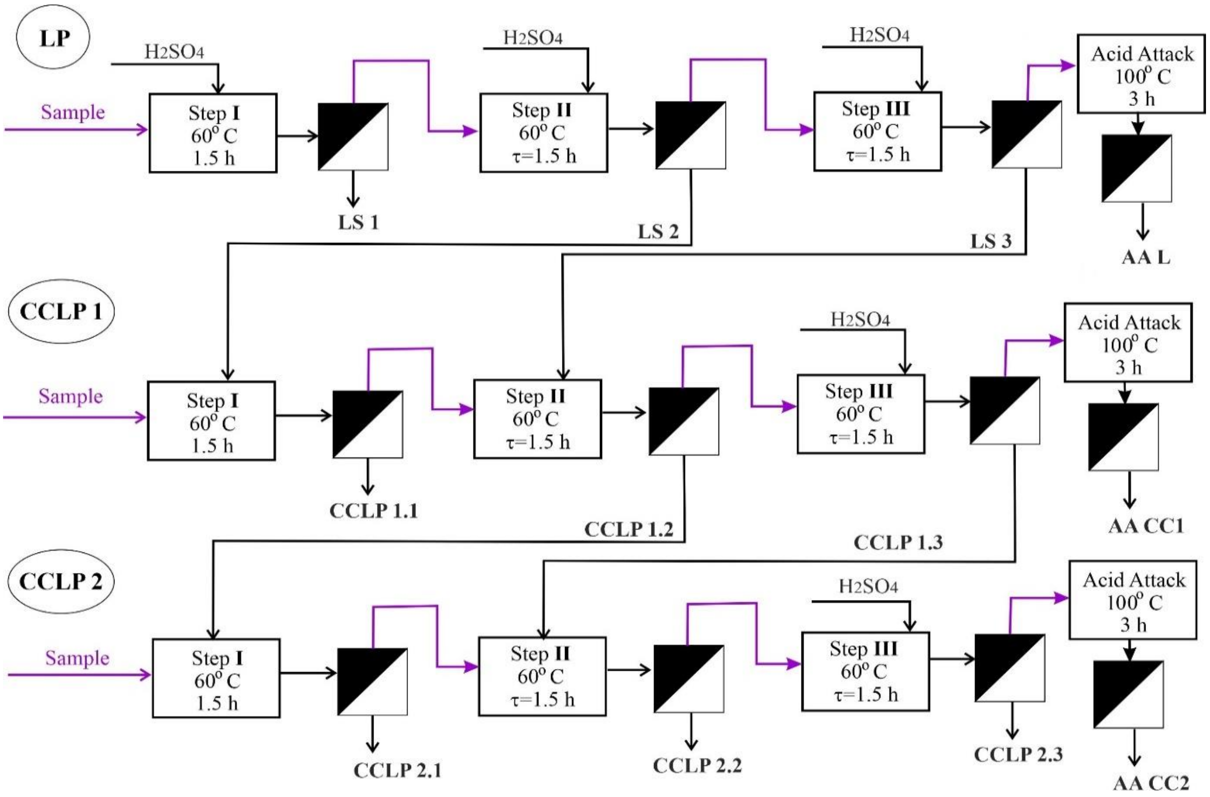

Figure 12. Flow chart of three step counter-current leaching process

Summarizing the following conclusions were made:

1. 2 step CCLP can be recommended for In dissolution from green ITO glass (Sample 2) by 0.5M sulfuric acid

2. 3 step CCLP can be recommended for In dissolution from green ITO glass (Sample 2) by 0.1M sulfuric acid
3. Process organization in three step CCLP with 0.1M sulfuric acid result in high In dissolution at low reagent consumption in comparing with current leaching process with acid recycling (0.5M) and 3 step CCLP (0.5M).

4.1.5 Conclusions

Comparative characteristics of the studied leaching processes presented in the Table 12.

Table 12. Comparative characteristics of the studied leaching processes

	pH	H_2SO_4, 96%, kg/t ITO glass	H_2O, kg/t ITO glass	In, mg/L	In recovery, %
Direct leaching (0.5M H_2SO_4)	0.7	343.8	6322.2	84.7	89.0
Cross leaching with acid recycling (0.5M H_2SO_4)	0.7	114.7	2107.3	449.6	83.0
2 step counter current leaching (0.5M H_2SO_4)	0.7	343.8	6322.2	168.7	99.9
3 step counter current leaching (0.1M H_2SO_4)	1.2	68.7	6597.3	211.4	99.8

Based on results of experiments most effective and feasible leaching scheme are:

a. Three steps counter-current leaching process with 0.1M sulfuric acid.
   pH of leaching solution 1.2
   H_2SO_4 (96%) consumption 68.6 kg/kg ITO glass
   Water consumption 6 597.3 kg/kg ITO glass
   In content in leaching solution ready for In recovery
      i. Sample 1: 7.4 mg/L
      ii. Sample 2: 211.4 mg/L

b. Three step cross leaching with acid recycling (0.5M sulfuric acid)
   pH of leaching solution 0.7
   H_2SO_4 (96%) consumption 114.6 kg/kg ITO glass
   Water consumption 2107.4 kg/kg ITO glass
   In content in leaching solution ready for In recovery
      i. Sample 1: 22.1 mg/L
      ii. Sample 2: 449.6 mg/L

The optimal leaching scheme should be chosen taking into account the possibility of further extraction of indium from the leaching solution. From this point of view 3 step counter current leaching with 0.1M sulphuric acid resulting in less acidic solution, less consume of sulphuric acid is most feasible.

The next task of the research was to study various processes for indium recovery by precipitation, ion exchange and electrolysis.

4.2. Recovery of indium

In this work, indium recovery from the Sample 2 CCLP (0.1M H_2SO_4) leaching solution, was investigated by precipitation with NaOH, electrowinning and ion exchange method.

4.2.1 Precipitation with NaOH

Experiments were carried out with leaching solutions after three step leaching with 0.5M acid recycling. It can be seen that the indium precipitation rate with sodium hydroxide increased with increasing pH of the solution (Table 13). Upon raising the pH to above 8, there is a nearly 100% reduction in the filterable phase of indium.

As it can be seen from the Figure 14 almost 5.4L and 5.5L of 1M NaOH required for neutralization of leaching solution (respectively Sample 1 and Sample 2) up to pH 8. Which corresponds to the consumption of sodium hydroxide 216 g/L (Sample 1) and 220 g/L (Sample 2).

Acid attack of Sample 2 precipitate (after drying at 105°C for 24h) did show 93.2% of In.

Table 13. Effect of pH value on precipitation of indium with NaOH

pH	Sample 1			Sample 2		
	In, mg/L	Sn, mg/L	In recovery, %	In, mg/L	Sn, mg/L	In recovery, %
0.7	22.1	4.6	0	449.6	25.7	0
2.0	22.1	3.3	0	449.4	17.7	0
3.0	21.3	0.4	5	395.6	5.4	12
4.0	15.0	0.1	32	256.3	0.3	43
5.0	12.4	<0.1	56	184.3	<0.1	59
6.0	5.7	<0.1	74.2	97.1	<0.1	78.1
7.0	2.5	<0.1	88.4	48.5	<0.1	89.2
8.0	**0.1**	**<0.1**	**99.5**	**1.3**	**<0.1**	**99.7**
9.0	0.04	<0.1	99.9	0.4	<0.1	99.9
10.0	0.04	<0.1	99.9	0.4	<0.1	99.9

The neutralization of sulfuric acid occurs in two stages:

$$H_2SO_4 \leftrightarrow HSO_4^- + H^+ \qquad (3)$$

$$HSO_4 \leftrightarrow SO_4^{2-} + H^+ \qquad (4)$$

Since sulfuric acid is strong, there is only one flex in the titration curve. In our case, the titration was carried out with help of Compact Titrator (G20S). Titration was carried out on a dilute solution (dilute solution of sulfuric acid), resulting in 2 flex in the curve - corresponding to two stages of hydrolysis.

The titration curve of pH versus NaOH titration volume (Figure 14) for H_2SO_4 (0.5M) before and after Sample 1 (LS_B) and Sample 2(LS_V) leaching demonstrate 2 inflection points found for each indicated transition (Figure 14). On the graphs, the consumption and concentration of sodium hydroxide are given in ml/L 1M NaOH.

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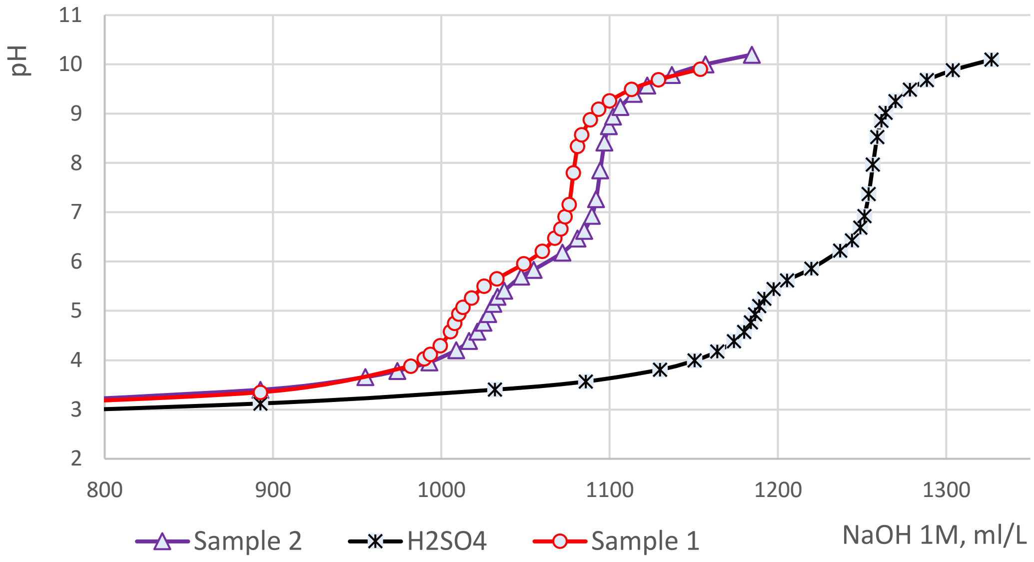

Figure 14. Potentiometric titration curves with 1M NaOH of 50 ml Leaching Solutions

As it was said before, in case of sulphuric acid titration, first and second equivalence point corresponding reaction (3) and (4). Titration curve of leaching solution (sulfuric acid after leaching Sample 1 and 2 of ITO glass) have the same shape with less consumption of NaOH.

Based on concentration and volume of the titrant (NaOH) we can estimate initial concentration of sulphuric acid:

$$N(H_2SO_4)=\frac{1M\ NaOH \cdot 1.027\ L}{1L\cdot 2}=0{,}51\ \text{mol/L}$$

And sulfuric acid content after Sample 1 leaching:

$$N(H_2SO_4)=\frac{1M\ NaOH \cdot 0.968L}{1L\cdot 2}=0{,}48\ \text{mol/L}$$

After Sample 2 leaching:

$$N(H_2SO_4)=\frac{1M\ NaOH \cdot 0.995\ L}{1L\cdot 2}=0{,}49\ \text{mol/L}$$

Based on the data obtained, it can be concluded that sulfuric acid is consumed insignificantly during leaching (its concentration decreases on 0.2 for Sample 2 and on for Sample 1 – 0.3M).

Due to the fact that the content of indium in the studied samples is several times lower than the content of sulfuric acid, there is no pronounced indium equivalence point on the titration curves. It can be assumed that it coincides with the second equivalence point of sulfuric acid.

Despite the fact that sodium hydroxide showed a high effect of indium precipitation, its huge consumption makes the method economically unfeasible.

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4.2.2 Electrowinning

The In electrowinning (EW) was carried out on Cu cathode and graphite anode in order to evaluate In recovery efficiency depending on pH of initial solution. The results of experiments (Table 14, Figure 16) indicate that In recovery efficiency depend on time and initial pH of leaching solution.

In case of electrowinning of the leaching solution of Sample 2 after leaching with 0.1M H_2SO_4 (pH=1.2), In removal effect after 2.5 h was almost 80.5 % (Figure 17). Instead in case of electrowinning solutions with initial pH 0.9 (0.3M H_2SO_4 leaching) and pH 0.7 (0.5M H_2SO_4 leaching) – 10 and 2% respectively.

Based on the results obtained, a real influence of the pH value on indium electrowinning processes has been observed. If the pH of the solution is too low, particles of H^+, or protons, also can be deposited onto the cathode, which negatively affects the extraction of metal. Increasing pH enhances the In deposition reaction and reduces the amount of hydrogen evolved, thus resulting in a higher current efficiency.

Table 14. Indium electrowinning efficiency from the Sample 2 at different pH.

Time, min	voltage, V	current, mA	Submerged surface, m^2	Current density, A/m^2	In, mg/L	In removal, %
pH=0.7 (leaching with 0.5M H_2SO_4)						
0	2.5	30	0.00103	29.1	169	-
30	2.5	29	0.00103	28.2	169	0.0
60	2.5	26	0.00103	25.2	168	0.6
90	2.5	24	0.00103	23.3	167	1.2
120	2.5	23	0.00103	22.3	167	1.2
180	2.5	21	0.00103	20.4	166	1.8
pH=0.9 (leaching with 0.3M H_2SO_4)						
0	2.5	40	0.00103	38.8	124	-
30	2.5	32	0.00103	31.1	122	1.2
60	2.5	26	0.00103	25.2	119	4.1
90	2.5	25	0.00103	24.3	115	7.1
120	2.5	24	0.00103	23.3	112	8.9
180	2.5	24	0.00103	23.3	101	19.1
pH=1.2 (leaching with 0.1M H_2SO_4)						
0	2.5	52	0.00103	50.4	211	-
30	2.5	40	0.00103	38.8	189	10.0
60	2.5	25	0.00103	24.3	168	20.5
90	2.5	20	0.00103	19.4	101	52.3
120	2.5	18	0.00103	17.5	65	68.8
180	2.5	17	0.00103	16.5	39	81.5

The main cathode reaction in deposition of indium:

$$In^{3+} + 3e^{-} = In^{0}(\downarrow)$$

Other possible reaction:

$$2H^{+} + 2e^{-} = H_2(\uparrow)$$

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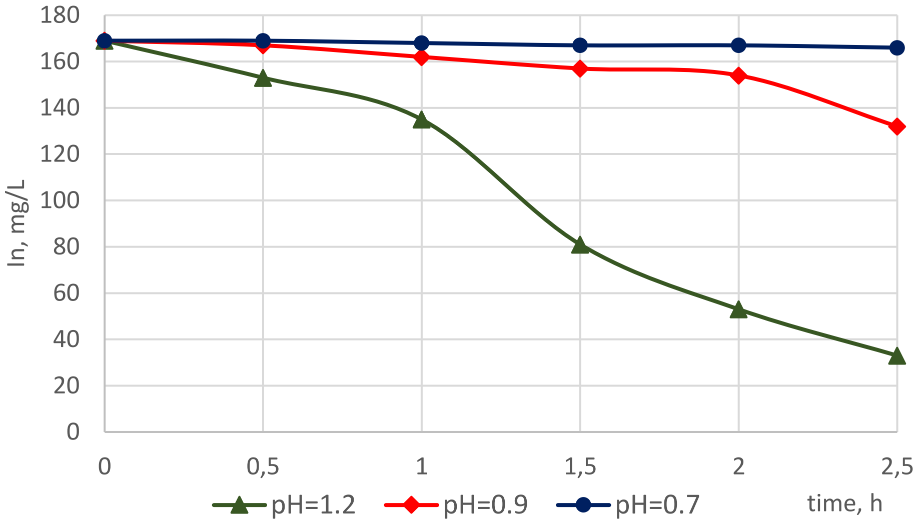

Figure 16. Effect initial pH of leaching solution on EW efficiency depending on time

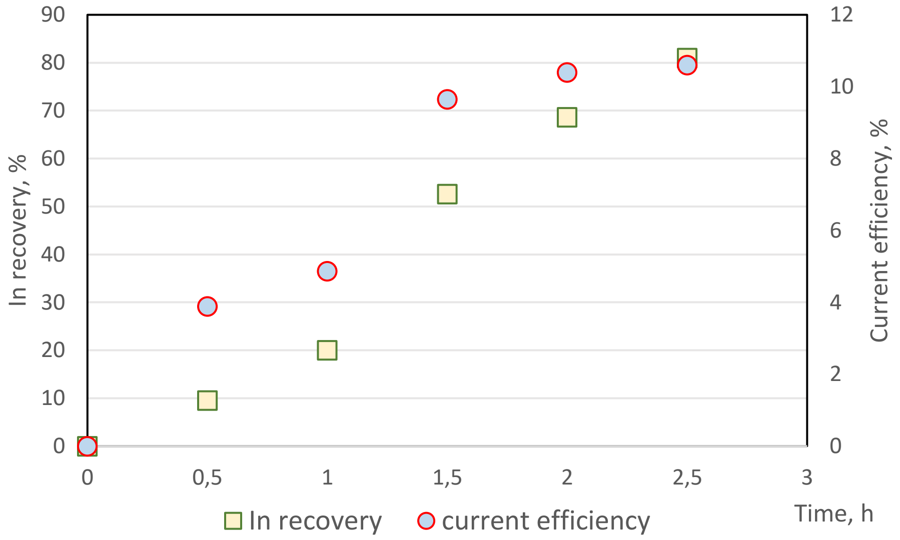

Figure 17. Effect of time on EW current efficiency (pH 1.2)

Finally, it is possible to state that Ni and SS are the most suitable cathodic supports for indium electrowinning from sulfate solution, nevertheless Ti cathode also present significative results and could be employed for further optimization investigations.

Therefore, the recovery of pure indium metal directly from indium containing leachate was achieved by consuming 15 kWh/kg In at pH 1.2.

4.2.3 Ion exchange

pH is one of the significant influencing parameters on the sorption behavior of ion exchange resins due to protonation and deprotonation of the acidic and basic functional groups of resins. Therefore, the pH dependence removal of the three ion exchange resins by varying the pH was studied while other parameters were kept constant (ambient temperature, time: 2 hours and loaded resin 1% w/v).

Three different pH (0.7, 0.9 and 1.2) after Sample 2 leaching with 0.5, 0.3 and 0.1M H_2SO_4 were tested in triplicate to evaluate the effect of pH to selectively bind indium. To determine this maximum exchange capacity, 0.5 g (1% w/v) of different kind of resins (Table 15), were brought in contact with 50 mL of leachate. The samples were stirred at 150 rpm for 2 h and then, filtered. These tests were carried out at room temperature.

Table 15. Characteristics of the ion exchange resins used in this study

	In, mg/L			
	Amberlite IRC 748	**Amberlite IRA 67**	**Amberlite IR 120+**	**Lewatit TP 214**
Resins types	Chelating Cation exchange	Weak Base Anion exchange	Chelating Cation exchange	Chelating Cation exchange
Functional groups	Iminodiaceti acid	Tertiary amine	Iminodiacetic acid	Thiourea groups
Particle size (mm)	0.50-0.65	0.50-0.75	0.68-0.83	0.50-0.55

Table 16 shows the removal efficiency of In from the leaching solution depending on pH (LS after leaching with 0.5, 0.3 and 0.1M sulfuric acid) and type of resin. The results obtained indicate that the pH plays important role in ion exchange process. It can be seen that for all studied resins increasing in pH of leaching solution results in increasing of In removal efficiency. For example, in case of Amberlite IR 120, its removal efficiency was 50% at pH 0.7, 77% at pH 0.9 and 99.8% at pH 1.2 under the same conditions.

Table 16. In and Sn content in LS after treatment with Ion exchange resins at different pH (1% w/v, 2 h, ambient temperature)

pH	Initial	Amberlite IRC 748	IRA 67	IR 120+	Lewatit TP 214
In, mg/L					
0.7	141.2	131.0	141.2	69.9	122.9
0.9	207.5	185.5	151.1	46.7	187.5
1.2	113.5	75.6	109.0	1.7	98.3
Sn, mg/L					
0.7	12.2	7.4	10.9	9.7	10.3
0.9	13.4	5.3	11.4	8.4	10.8
1.2	1.7	0.4	1.7	0.5	1.2

The resins were classified based on the maximum percentage of indium fixed at pH 1.2 as following:

IRA 120+ (98.5%) > IRC 748 (33.4%) > TP 214 (13.4%) > IRC 748 (53.2%) > IRA 67 (3.9%).

Figure 18 shows the removal percentage of In(III) as a function of pH for Amberlite IR 120 in the range of 1 and 0.5% w/v. As can be seen, that increasing of resin dosage in 2 times (from 0.5 to 1% w/v) resulting in increasing adsorption of In:

- at pH 0.7 on 17%
- at pH 0.9 on 14%
- at pH 1.2 on 1%

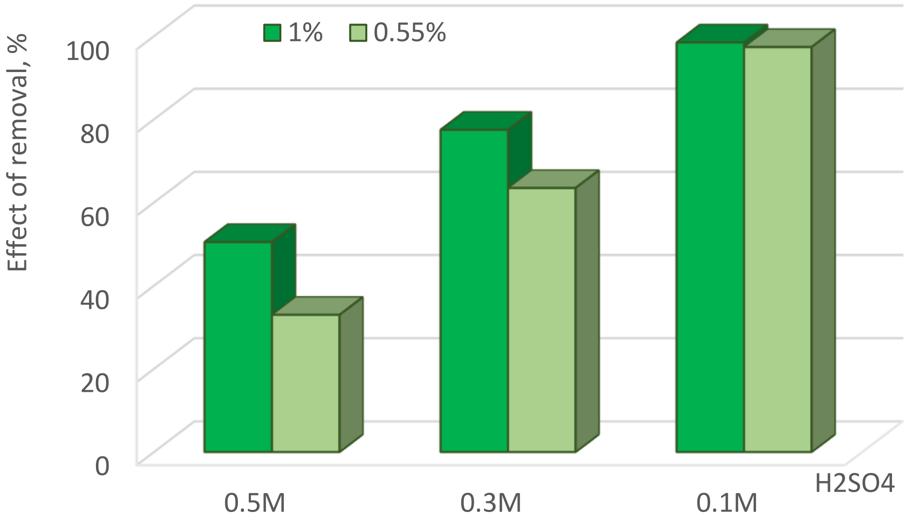

Figure 18. Effect initial pH of leaching solution on adsorption efficiency with Amberlite IR 120+

It is evident that the adsorption efficiency of indium using Amberlite IR 120 is feasible, at pH 1.2 which results in high removal efficiency (98%) at low resin dosage (0.5% w/v).

Concentrating of In(III) leachate could be obtained by adsorption/desorption process.

According **Fortin-Lecomte et al. (2022)**, the amount of In(III) eluted from the resin are 1.5 times higher with HCl as eluent compared to that with H_2SO_4. A 16%-increase in the elution of indium occurred with the increase of HCl concentration between 1 M (78%) and 3 M (94%). The most efficient elution of indium with HCl is observed at a concentration of 7 M (102%). Herein, HCl (2 M) could effectively desorb In(III) from the loaded resins in a short time of 5 min. Instead considering H_2SO_4 as eluent, it can be noticed that the elution for indium is 61% with 5 M H_2SO_4.

4.2.4 Conclusions

Comparative characteristics of the studied methods for extracting indium are presented in the Table 17.

Table 17. Comparative characteristics of the studied In recovery processes

	pH	In recovery, %	Residual In in LS, mg/L
Precipitation	8.0	99.7	1.3
Ion exchange	1.2	98.3	1.7
Electrowinning	1.2	80.5	33.1

Although precipitation and ion exchange maximize the recovery of indium from the leaching solution, these methods require further processing to obtain saleable indium. In contrast, the extraction of indium by electrolysis makes it possible to obtain a final product that does not require further processing. An analysis of the literature shows that the use of electrolysis under industrial conditions makes it possible to deposit almost 99% of indium from sulfate solutions. The low percentage of recovery (80%) in our case can be explained by the limited capabilities of the experimental setup, and anyway the residual solution can be recycled.

Based on results of experiments Electrowinning (EW) can be recommended for In recovery from leaching solution after 3 step CCLP with 0.1M sulphuric acid.

Material balance are given in the Table 18.

Table 18. Mass balance for EW recovery of In from Sample 2, 3 step CCLP (0.1M H_2SO_4)

INPUT		OUTPUT	
Description	kg	**Description**	kg
Leaching solution for In recovery	6702	Leaching solution after EW	6700.85
		In	1.15
Total	**6702.0**		**6702.0**

4.3. Spent washing water treatment

Sample 2 washing water parameters allow it to be recycled without purification, while Sample 1 waste washing water need to be treated.

Fenton's reactions were examined at optimal pH, H_2O_2 and Fe^{2+} concentration. The pH and reaction time was fixed during the treatment (Figure 19). Sample 1 spent washing water (after 3 cycles) was taken for the treatment.

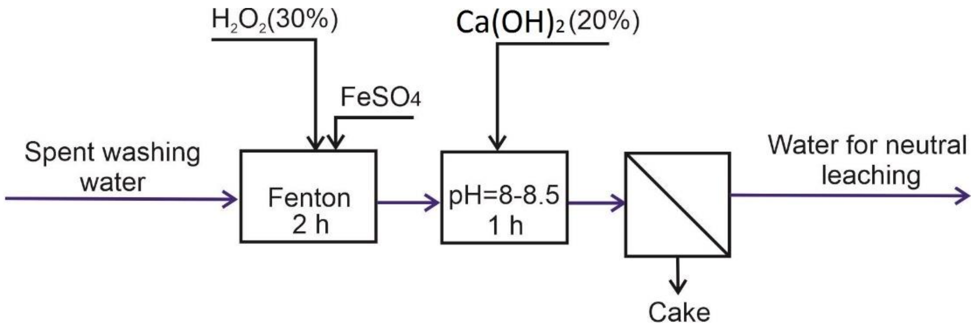

Figure 19. The block diagram of the AOP (Fenton process for Sample 1 spent washing water treatment)

Sample 1 spent washing water after neutral leaching was COD = 1.65 g/L, TSS = 0.465 g/L and pH=6.1.

Calculated amount of $FeSO_4 \cdot 7H_2O$ was added to the reaction solution as the ferrous iron source and temperature was fixed at 30^0C. The reaction was assumed to start with the addition of H_2O_2. All experiments were carried out for 2 h of reaction time.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101003587

After what $Ca(OH)_2$ 20% wt/wt was added until the pH became 8.0-8.5 for precipitation conditions.

COD and TSS removal efficiencies obtained after Fenton's treatment of wastewater were 98 and 90% respectively. The mass of precipitate after filtration and drying at 105°C for 24h was 1.98 kg/m^3.

Reagent consumption of studied Fenton process are shown in the Table 19.

Table 19. Reagent consumption of spent washing water treatment by AOP

Step	kg/m^3 spent washing water			
	H_2O	H_2O_2, 30%	$FeSO_4$ $7H_2O$	$Ca(OH)_2$
AOP	-	4.8	6.1	-
Neutralization up to pH=8	-	-	-	41

Material balance are given in the Table 19.

Table 19. Mass balance AOP (spent washing water treatment after 3 cycles of neutral leaching)

INPUT		OUTPUT	
Description	kg	**Description**	kg
Spent washing water	1000	Treated washing water	1006.1
$Ca(OH)_2$	41	Sludge (water content 60% wt/wt)	67
H_2O_2 (30%)	5		
Fe_2SO_4	6.1		
Water	21		
Total	**1073.1**		**1073.1**

4.4. Spent leaching solution treatment

After the extraction of indium from the spent leaching solutions, the step of their purification is necessary.

The most common method for removing high concentrations of sulfate from water is through addition of hydrated lime ($Ca(OH)_2$), which precipitates calcium sulfate:

$$H_2SO_4 + Ca(OH)_2 \Rightarrow CaSO_4 + 2HOH$$

Calcium sulfate, which hydrates to become the common mineral gypsum, has a solubility of approximately 2000 mg/L as sulfate. Sulfate reduction below 2000 mg/L has been possible in the past only through expensive technologies such as reverse osmosis (RO) or ion exchange (IX). Large volumes of liquid waste are generated with RO and IX, which typically create additional treatment and disposal costs. The CESR process can reduce the sulfate concentration in most wastewaters to less than 100 mg/L through use of a proprietary powdered reagent.

ttps://www.wateronline.com/doc/a-new-process-for-sulfate-removal-from-indust-0001

A mixing time of 40 to 60 minutes is adequate for initial sulfate precipitation. The sulfate content of the wastewater can be lowered to 4000 to 5000 mg/L, with the resulting gypsum easily dewatered in a filter or belt press. Approximately 1.8 kg of gypsum are precipitated per kg of sulfate. Since this is pure gypsum, no special handling or disposal permits are required.

During the precipitation step, 20 % $Ca(OH)_2$ was gradually added to Sample 2 solution after recovery of In (EW) under constant stirring until reaching the around desired pH. The mixture was stirred further for 2h to ensure precipitation equilibrium. Precipitation tests were performed in a pH range of 5-7, at room temperature (25±2 °C). The final pH was then measured, and the precipitate was separated from the slurry by centrifugation. For each considered pH, the obtained filtrate was analyzed for determining the residual COD, In and Sn.

Results of experiments are presented in the Table 20.

Table 20. Quantitative analysis of wastewater (Sample 2) before and after treatment with lime at different pH

Step	Before precipitation	After precipitation with lime		
pH	1.2	4.9	6.2	7.5
Ca, mg/L	12.5	137.6	198.7	214.8
SO_4	9600	9250	3790	2000
COD, mg/L	36	36	32	29
In, mg/L	33.1	7.5	3.8	0.5
Sn, mg/L	9.6	0.5	0	0

Material balance are given in the Table 21.

Table 21. Mass balance for lime neutralization process of spent leachate after 3 cycle CCLP (3 step 0.1M H_2SO_4)

INPUT		OUTPUT	
Description	kg	**Description**	kg
Acid waste water	1000	Treated acid waste water	895
$Ca(OH)_2$	**37**	Sludge (water content 60% wt/wt)	327
Water	185		
Total	**1222**		**1222**

5. Process analysis

Based on the experimental results of the experiments carried out in the analysis of the process of extracting indium from waste ITO glass, in accordance with the scheme presented in Figure 20.

This chapter presents sections describing the process, mass balances and assessing the feasibility of the process from an environmental and economic point of view.

5.1. Process flowsheet

The complex process for two samples of ITO glass was described in sections 4.1 (Indium leaching), 4.2 (Indium recovery) and 4.2-4.3 (treatment of generated liquid waste).

As it can be seen from Figure 20, the process includes three main stages:

a. *Neutral leaching.* Pretreatment of ITO glass by washing with water in order to remove impurities and liquid glass.
b. *Acid leaching.* Three steps counter-current leaching process with 0.1M sulfuric acid for Indium dissolving.
c. *Indium electrodeposition* by electrowinning process.

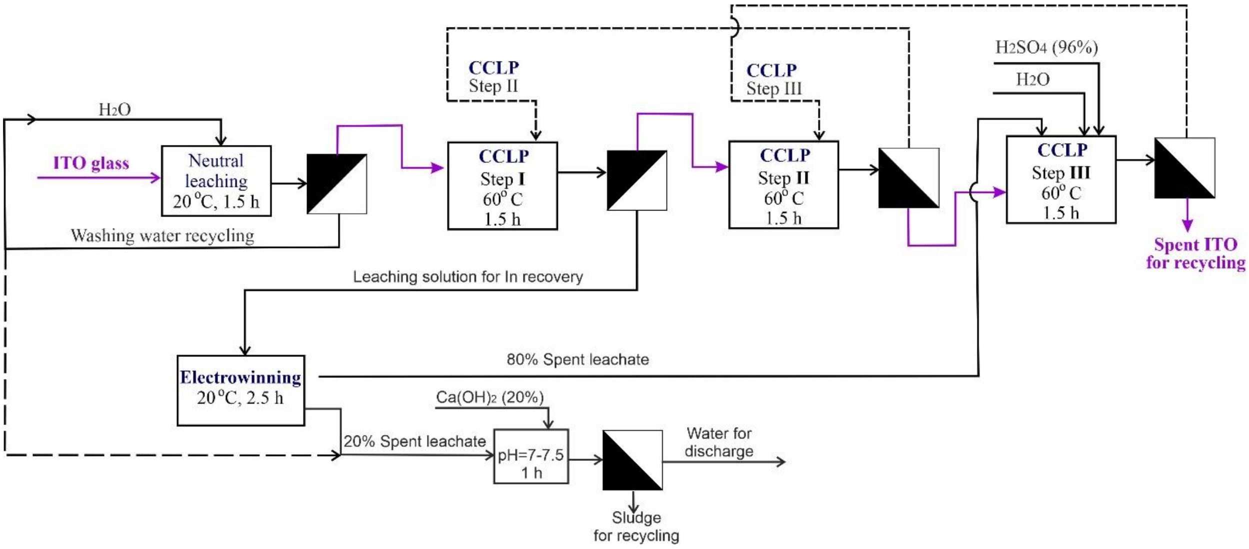

Figure 20. Scheme of the process of extracting indium from ITO glass waste (Sample 2)

In addition to the three main stages of the indium extraction process, 2 types of liquid waste are generated: wastewater after neutral leaching and acidic wastewater.

Parameters of first one (spent washing water), as COD, Suspended Solids mainly depend on the type of ITO glass being processed. In the case of a Sample 1, an effluent treatment process is required after 3 recycles. In the case of Sample 2, the rinsing process practically does not lead to water pollution.

Considering the low content of Indium in the Sample 1 (60-70 g/t - in front of 925-1890 g/t in the Sample 2), formation of waste washing water with the need to use the Fenton process for its purification, further calculations presented in this section was made for the process of extracting indium from Sample 2. Therefore, spent washing water treatment process (Section 4.3) is not included into the general process presented in the Figure 20.

Instead, the step of acid wastewater (spent leaching solution) treatment included in the general scheme and follows the processes of electrowinning. Water after treatment can recycled.

In addition, 2 types of solid waste are formed - waste glass after the extraction of indium and sediment after cleaning the waste leaching solution.

In Table 22, the results in terms of silver recoveries are reported for each step of the process.

Table 22. Summary of the obtained results in terms of Indium recovery

Process step	In, %
Neutral leaching	0
Three step counter current leaching	99.8
Electrowinning	80.5

Summing up, the proposed scheme for the extraction of indium includes its dissolution and electrodeposition. Adopting the proposal process to processing of ITO glass Sample 2 with an average content of indium equal to 0.12 wt %, operating at a solid concentration of 15 % w/v, an Indium dissolution of 99.8 % can be achieved after three steps of counter-current leaching. The recovery of Indium obtained by electrowinning, 80.5%, is closely linked to the equipment used. Generally, industrial-scale electrowinning achieves recoveries of more than 95 %.

5.2 Mass balances

Based on the experimental results, mass balances referred to the hydrometallurgical process of 1 ton of Sample 2 of ITO glass are reported in Table 23 (A and B). The mass balances are calculated according to the process with three steps of treatment (neutral and acid leaching, EW) with the treatment of spent leaching solution by neutralization and its recycling.

Table 23. Mass balance of the process of extracting indium from ITO glass waste (Sample 2)

A. Starting Regime

INPUT, kg		OUTPUT, kg	
Neutral leaching (Washing with H_2O)			
Solid (ITO glass)	**1000.0**	Solid (ITO glass)	**995.0**
Water	6666.0		6671.0
Total	**7666.0**		**7666.0**
3 step CCLP (0.1M H_2SO_4)			
Solid (ITO glass)	**995.0**	Solid (ITO glass)	**938.0**
H_2SO_4, 96%	206.1	Leaching solution for In recovery	6527.0
Water	19791.9	Leaching solution for recycling	13528.0
Total	**20993.0**		**20993.0**
Electrowinning			
Leaching solution for In recovery	**6527.0**	Leaching solution after EW	**6525.88**
		In	**1.12**
Total	**6527.0**		**6527.0**
Spent leachate neutralization			

Leaching solution after EW (20%)	**1305.2**	Treated acid waste water for recycling	1166.8
$Ca(OH)_2$	48.4	Sludge (water content 60% wt/wt)	428.4
Water	241.6		
Total	**1595.2**		**1595.2**
Total			
	36781.2		**36781.2**

B. Working Regime

INPUT, kg		**OUTPUT, kg**	
Neutral leaching (Washing with H_2O)			
Solid (ITO glass)	**1000.0**	Solid (ITO glass)	995.0
Water	1333.0	Recycled solution for neutral leaching	1338.0
Total	**2333.0**		**2333.0**
3 step CCLP (0.1M H_2SO_4)			
Solid (ITO glass)	**995**	Solid (ITO glass)	**938.0**
H_2SO_4, 96%	34.2	Leaching solution for In recovery	6527.0
Water	1077.7		
Recycled Leaching solution after EW (80%) for step 3	5220.8		
Recycled leaching solution for step 2 and 1	13265.4	Recycled leaching solution	13128.1
Total	**20593.1**		**20593.1**
Electrowinning			
Leaching solution for In recovery	**6527.0**	Leaching solution after EW	**6526.0**
		In	**0.00112**
Total	**6527.0**		**6527.0**
Spent leachate neutralization			
Leaching solution after EW (20%)	**1305.2**	Treated acid wastewater for disposal	1166.8
$Ca(OH)_2$	48.4	Sludge (water content 60% wt/wt)	428.4
Water	241.6		
Total	**1595.2**		**1595.2**
Total			
	31048.3		**31048.3**

The powder amount recovered from the cathode is referred only to the Indium, considering minor concentrations of other metals compared to indium (<0.1%).

Expected Indium amount in the powder is 1.12 kg, Finally, treated wastewater output for recycling is 6.865 t and formed during lime neutralization sludge is 1.109 t (water content 60% wt/wt).

5.3 Outputs characterization

In the present section, the following outputs were characterized to evaluate their management better:

a) solid residue
   - sludge after spent leaching solution neutralization with lime
   - spent ITO glass after 3 step counter current leaching process

b) powders from the electrowinning

c) wastewater

- acid wastewater for lime neutralization and recycling
- spent wastewater after neutral leaching for recycling

5.3.1 Solid output products

Main characteristics of solid output products are presented in the Table 24.

I. The sludge formed after lime neutralization of spent leaching solution (water content 60% wt/wt) was dryed at 105^{0}C for its dewatering and resulting powder of gypsum dihydrate ($CaSO_4{\cdot}2H_2O$).

Table 24. Composition of the sludge after neutralization with lime and after 105°C thermal treatment (XRF)

Elements	wt %
Ca	49.9
S	8.2
In	<0.1
Sn	<0.1

According obtained data $CaSO_4{\cdot}2H_2O$ content in obtained sludge after thermal treatment was 84.4%. Lime sludge after neutralization in its raw form, depend on chemical composition, may fit for use in other industries:

- in construction to produce concrete and bricks
- in processes like compounding and sand washing when manufacturing glass

II. The spent glass parameters after EW.

Typical chemical composition of LCD glass (60.82% SiO_2, 16.29% Al_2O_3, 10.22% B_2O_3, 9.49% CaO, 8.44% Na_2O, 1.83 MgO, 1.08% K_2O, and 0.04% Fe_2O_3) satisfies the chemical requirements for a pozzolanic material (defined by its ability to react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties), as specified in ASTM C618, 2019. Moreover, most of the chemical compounds are present in an amorphous phase and spent LCD glass can be added as a general waste during concrete production.

LCD glass meets the Environmental Protection Agency's limitations for some metals The toxic characteristic leaching procedure (TCLP) regulatory limits, according Test Methods for the

Evaluation of Solid Waste (1992), are: As – 5 mg/L; Cd – 1 mg/L; Cr_{total} – 5 mg/L; Hg – 0.2 mg/L; Ag – 5 mg/L; Cu – 25 mg/L; Pb – 5 mg/L; Ni – 20 mg/L; Zn – 250 mg/L.

The characterization of the ITO glass after In recovery confirmed the full recyclability of such waste glass as a pozzolanic material. Spent glass can be repurposed by open-loop system as raw material for production of:

- glass-ceramic tiles. After crushing, grinding and sieving at 16 mesh, the glass powder was heated up at 800–950 °C for 6 h (**Lin et al., 2009**)
- ceramic tiles (**Kim et al., 2016**)
- partial replacement for cement powder in mortar production (**Wang, 2011**)
- filler replacement in cement-based materials as fine or coarse aggregate in mortar or concrete (**Harrison et al. 2020**).
- as a new alternative ingredient for concrete, as a replacement for cementitious materials or sand (**Doo-Yeol Yoo et al., 2022**)

III. Powder recovered after EW.

It has be noted that given the small quantities obtainable on the laboratory scale, powder composition could be affected by experimental errors. This could therefore be an impurity closely related to the equipment used on a lab scale.

Therefore, for more assessments, it is necessary to consider the powder obtainable on a pilot scale.

5.3.2 Wastewater output products

Spent leaching solution composition after neutralization with lime is reported in Table 25.

Table 25. Composition of spent leaching solution (acid wastewater) before and after neutralization.

Parameters	Before	After
pH	1.2	7.5
Ca, mg/L	12.5	214.8
SO_4, mg/L	9600	2000
In, mg/L	33.1	0.5
Sn, mg/L	9.6	0
COD, mg/L	36	29

Experimental results show that after neutralization of acid wastewater with lime up to a pH 7.5, it can be recycled for preparation of leaching solution as well as for other purposes in the plant.

5.4 Economic and environmental evaluations

Economic evaluations on the silver recycling process are done based on the balance materials, calculated by experimental lab tests, and referred to a treatment of 1 ton of ITO glass.

Pending a more reliable result about the silver purity of the obtained powder, which can be provided from the pilot tests, for now, a 20 % of In value depreciation was considered for the preliminary economic analyses. Table 26 shows the chemical costs for the treatment of 1 ton of ITO glass.

Table 26: Chemical consumptions and costs for the treatment of 1 ton of ITO glass (Sample 2). Regime.

Chemical	Amount, t	Cost per unit, €/kg	Cost, €/t of ITO glass
Neutral leaching			
Washing water	1.333	0.0015	0.0019
Acid leaching			
H_2SO_4, 96%	0.066	0.26	17.16
Water	0.245	0.0015	0.00036
Spent LS neutralization			
$Ca(OH)_2$	0.121	0.15	18.15
Water	0.604	0.0015	0.0009
			35.3 €/t

Regarding energy consumption, the developed process for the treatment of ITO glass can be developed in a plant that requires the following consumption: stirring for the leaching operations and for the preparation of the solutions, pumps to discharge the chemical reactors and to separate the leach liquor from the solid residue, and the energy consumption for the indium electrodepositions, that is 15 kWh/kg. metals. Table 27 shows the energy consumption for each specific operation.

Table 27: Energy consumption.

Operation	kWh
Stirring	20
Pumps	24
Acid leaching (heating up to 60°C for 2.5 h)	195
In electrowinning (15 kWh/kg)	17
	256 kWh

Table 28: OPEX for the treatment of 1 ton of ITO glass with 80% recycling of spent solutions.

Item			Cost, €/ton of ITO glass
Chemicals	details are reported in Table 26		17.1
Energy consumption	kWh	€/kWh	92.1
	256	0.36	

Wastewater Treatment	m^3	€/m^3	18.2
	1.3	14	
Sludges of wastewater treatment	kg	€/kg	-
	428.4	To be evaluated	
			127.4 €/t

Regarding revenues, currently, for indium is considered the quotation value of 213 €/kg. Solid residue of ITO glass is composed of glass, currently has not been considered either as revenues and nor as a cost, it can be defined after having evaluated the requirements. In any case, this is a critical step because it is totally dependent on the purity obtainable. Purities could be determined after the scale-up of the process.

Based on these considerations, the process revenue is 249,8 €/ton. Therefore, subtracting OPEX, you have a **122.4 €/ton profit**. For a more detailed economic analysis, pilot-scale tests will allow us to estimate the revenues in a certain way and to define the profit margin from the treatment of ITO glass.

6. Conclusions

With the aim of studying the optimization of the hydrometallurgical process for the recycling of Indium from ITO glass, the following results have been achieved:

a. Chemical characterization based on the studied ITO glass chemical attack and ICP-OES analysis of resulting solution demonstrate that Indium is present with the following contents:
    i. Sample 1: In 0.007 wt %
    ii. Sample 2: In 0.12 wt %

   The difference in In content can be explained, by difference in the thickness of ITO layer: Sample 1 – 30±5nm; Sample 2 – 350±30nm.
   The other element, most present in both samples' elements was silicon (>30% wt). As regards those detected at lower concentrations were manganese, calcium, and sulphur.

b. The hydrometallurgical process includes two stages of neutral and acid leaching, with subsequent extraction of indium by electrodeposition on a copper cathode. The optimal ratio of solid and liquid fraction for leaching is 1.5/10 (15% wt/v)

c. Neutral leaching stage (section 4.1.1):
    i. In case of Sample 1 ITO glass, neutral leaching is essential pretreatment process. Spent washing water can be recycled maximum 3 times after what has to be treated by Fenton process with further neutralization and filtration.
    ii. In case of Sample 2, the washing water formed during the experiments did not require purification and could be used at least 10 times. The final decision on the practicability of the neutral leaching stage and resulting wastewater treatment, should be made after pilot testing.

d. For the process optimization of the acid leaching operations, different scenarios were studied:

   i. One step direct leaching by 1M sulfuric acid, resulting in 99.3 % of In dissolution has been achieved with maximum In content in leaching solution of 5.1 and 92.1 mg/L for Sample 1 and Sample 2 respectively (Treasure section D5.3).
   ii. Two step cross leaching (0.5M sulfuric acid) with acid recycling. In this case, about 83 % of In dissolution has been achieved with maximum In content in leaching solution of 22 and 450 mg/L for Sample 1 and Sample 2 respectively (section 4.1.3).
   iii. Three steps counter-current leaching process with 0.1M sulfuric acid. In this case, about 99.8 % of In dissolution has been achieved with maximum In content in leaching solution of 7.4 and 211 mg/L for Sample 1 and Sample 2 respectively (section 4.1.4).

e. Considering low In content and the need for additional physicochemical treatment of washing water after neutral leaching, Sample 1 processing for Indium recovery is not feasible.
f. The optimal leaching scheme for Sample 2 processing was chosen considering less energy consumption and the possibility of further extraction of indium from the leaching solution. From this point of view, the most feasible is three-step counter current leaching by 0.1M sulfuric acid, resulting in a less acidic solution (pH=1.2) and almost two times less sulfuric acid consumption at a higher In extraction yield (99.8 %).

g. Electrowinning (EW) can be recommended for In recovery from leaching solution after 3 step CCLP with 0.1M sulphuric acid (section 4.2.2).

h. The energetic consumption of In electrowinning is in the range of 15 kWh/kg based on the different tests, with a Indium recovery after 2.5 hours of 80.5 %.

i. Acid wastewater (spent leaching solution) is mainly composed of SO_4 (about 3.22 g/L); the other elements detected are Indium (33.1 mg/L), tin (9.6 mg/L) and calcium (12.5 mg/L). 80% of spent LS after EW can be recycled in CCLP (Figure 20). Treatment of remaining 20% can be carried out by calcium hydroxide neutralization (section 4.4).

j. Economic sustainability studies, by assuming a treatment of 1 ton of ITO, show that OPEX is 127.4 €/ton. Specifically, 17.1 €/ton for the chemicals, 92.1 €/ton for the energetic consumption, and 18.2 €/ton for the treatment of wastewater, the revenue from In sale is 249,8 €/ton. Therefore, the process profit is 122.4 €/ton.

Abbreviations

AOP	Advanced oxidation Process
CCD	Central composite design
CCLP	Counter-current leaching process
CLP	Cross leaching process
COD	Chemical oxygen demand
CRM	Critical raw material
EW	Electrowinning
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
ITO glass	Indium Tin Oxide coated glass
LCD	Liquid crystal display
LS	Leaching solution
MLD	Minimum Liquid Discharge
OPEX	Operative Expenses
TSS	Total Suspended Solids
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

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