sustainability

MDPI

Article

Recovery of Metals from Printed Circuit Boards by Gold-REC 1 Hydrometallurgical Process

Nicolò Maria Ippolito *, Marco Passadoro, Francesco Ferella, Giorgio Pellei and Francesco Vegliò

Department of Industrial and Computer Engineering and Economics, University of L'Aquila, 67100 L'Aquila, Italy; marco.passadoro@graduate.univaq.it (M.P.); francesco.ferella@univaq.it (F.F.); giorgio.pellei@student.univaq.it (G.P.); francesco.veglio@univaq.it (F.V.)

* Correspondence: nicolomaria.ippolito@univaq.it

Abstract: The paper describes a small full-scale plant based on the Gold-REC 1 process, designed and patented by the University of L'Aquila; the hydrometallurgical process allows the treatment of printed circuit boards (PCBs). The first step is a mechanical treatment to reduce the size of the scraps below 2 mm. The extraction of base metals occurs in a first reactor by a sulfuric acid/hydrogen peroxide solution. After filtration, the solid is leached again with thiourea and ferric sulfate in a sulfuric acid solution to extract gold and silver. This second solution is sent to an electrolytic cell where gold is recovered as metal powder. The resulting solution undergoes a second electrowinning, where silver is deposited on the cathode. The first pregnant solution undergoes recovery of Cu and Sn. A simulation was developed using lab-scale trial results. The 350 tons PCBs/year, running in a batch operating mode, produces around 43.8 kg/year of gold, 85.8 kg/year of silver, 42.4 tons/year of copper, and 7.2 tons/year of tin oxide. The results show the profitability of the process: the net present value is EUR 10.7 M, with an internal rate of return of 150% and a discounted payback time of 2 years.

Keywords: PCBs; WEEE; recycling; gold; copper; electrowinning; countercurrent leaching; circular economy

Citation: Ippolito, N.M.; Passadoro, M.; Ferella, F.; Pellei, G.; Vegliò, F. Recovery of Metals from Printed Circuit Boards by Gold-REC 1 Hydrometallurgical Process. *Sustainability* **2023**, *15*, 7348. https://doi.org/10.3390/su15097348

Academic Editor: Eleni Iacovidou

Received: 10 March 2023
Revised: 24 April 2023
Accepted: 26 April 2023
Published: 28 April 2023

1. Introduction

The increasing generation of waste from electrical and electronic equipment (WEEE) reached a considerable amount in the last ten years, especially in economically developed countries. The growth of such wastes is directly proportional to the fast development of microelectronic technologies that quickly make personal computers (PCs), mobile phones, and other electronic devices obsolete [1]. The trend is unsustainable for two reasons: using natural resources to extract the necessary metals produces a considerable amount of harmful waste that must be disposed of properly. Metals on which these electronic technologies are based are not inexhaustible. In addition, ore deposits are located in a few countries such as China, Russia, South Africa, and Australia. This is an urgent problem in terms of supply, as well as looking at the geopolitical tensions that have arisen in the last two years.

Hence, WEEE represents the best example of urban mining. It contains base and precious metals that can be extracted and reused; the additional advantage is that their concentration is usually much higher than in primary ores and requires less energy for processing [2]. Printed circuit boards (PCBs), connectors, and others from medical, military, and research devices contain a significant number of precious metals, in particular, gold (Au), silver (Ag), and palladium (Pd), besides copper (Cu) and tin (Sn). Furthermore, PCBs are the sole WEEE whose recycling is feasible without any disposal fee due to the amount and value of the metals contained therein [3].

Nevertheless, PCBs contain around 70% wt of plastic–ceramic materials, glass fibers, such as epoxy resins, and brominated compounds used as flame retardants [2].

Spent PCBs are divided into categories depending on the particular WEEE they come from (mobile phones, PCs, military devices, TVs, washing machines, air conditioning units, copy machines, etc.). As a result, the precious metal content is quite different, making the profitability of PCB recycling almost variable [4,5].

The pretreatment stages are crucial for separating the metallic fraction from the inert one in an efficient way and to enhance the subsequent recovery [6,7].

The most used recycling techniques at a commercial scale are preferably based on pyrometallurgy, which removes the plastic board and concentrates metals in the char [8]. Nevertheless, several hydrometallurgical processes have also been studied: those using thiourea or other nontoxic mixtures such as $HCl/H_2O_2/CH_3COOH$ [9–11] are the most common. Instead, thiocyanate-based systems are hazardous and require additional safety measures [9].

Many processes have been investigated worldwide to extract metals from PCBs, mainly on a lab scale and a few on a pilot scale [12–22]. Considering the circular approach of the whole recycling concept, even the recovery of the nonmetallic fraction of PCBs has been studied [1]. Tantalum capacitors are components particularly better separated in advance for a more efficient recovery of tantalum and the primary metals of the PCBs [23].

Economic analyses have already been carried out on recycling processes. D'Adamo et al. demonstrated that the net present value (NPV) varies from EUR 6.8 M for medium-grade PCBs to EUR 63.0 M for high-grade PCBs, whereas it is negative for low-grade ones [1]. Another research work, which assessed the Australian scenario, concluded that a plant with 10,000 tons/year capacity would be sufficient to treat the current annual collected PCB in Australia; a lower capacity would result in an even higher economic feasibility [24]. Focusing on processes using thiourea for Au extraction, most of them have been applied to recover gold from primary ores; the final recovery has usually been carried out by electrodeposition [25–30].

The novelty of this paper can be placed on the technical and economic analyses of a plant treating 350 tons/year of PCBs focused on a new process aimed at recovering the most valuable metals, namely Cu, Sn, Au, and Ag. Apart from the technical simulation, a profitability analysis was also developed [31] using a modified version of the Gold-REC 1 process [32], patented by Birloaga et al. [33]. The original patented process indeed differs from this by the recovery methods used for Cu, Au, and Ag. While metastannic acid is always recovered by precipitation with a polyamine flocculant, copper and the precious metals are precipitated together by cementation with powdered zinc.

The process presented in this paper has been tested in the ambit of Treasure, a project funded by the European Commission under the Horizon 2020 program (grant agreement N.101003587).

2. Materials and Methods

2.1. Description of the Process

The flow sheet of the modified Gold-REC 1 is shown in Figure 1. This process is characterized by a two-stage leaching section: 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. This selective leaching is very helpful in separating metals already in the leaching section: this allows the efficient recovery of all of them in terms of total mass and grade. After the first leaching stage, the PCBs' solid undergoes a 24% weight reduction.

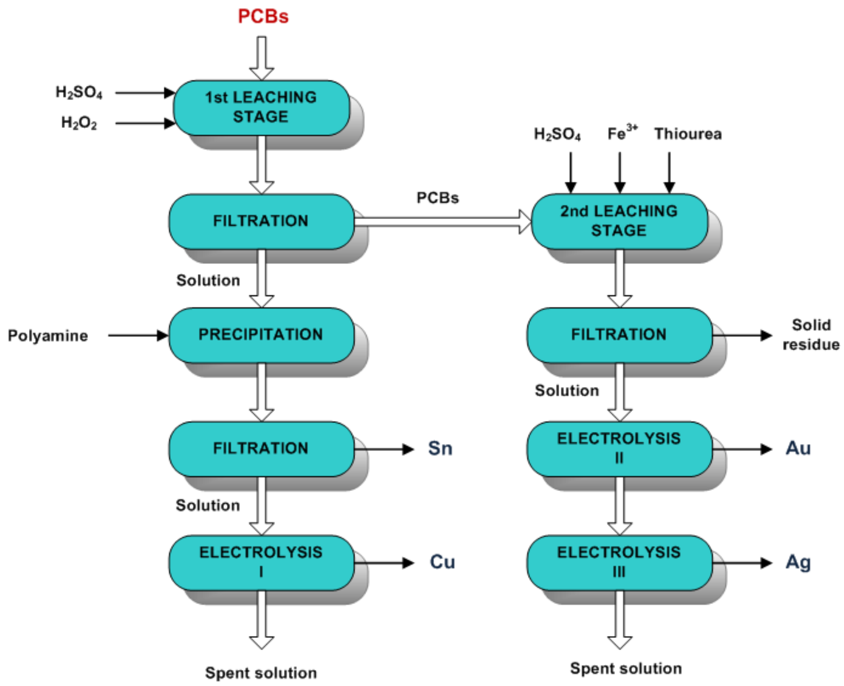

Figure 1. Gold-REC 1 recycling process flow-sheet.

Tin is precipitated by flocculation with the aim of polyamine in the form of metastannic acid (H_2SnO_3), whereas copper is recovered by electrodeposition. The spent solution is partially recycled back to the leaching reactor, and the rest is discharged after wastewater treatment to recover water. The second pregnant solution after the thiourea leaching undergoes sequential electrodeposition of gold and then silver under different operating parameters. The spent solution is thus recycled in the second leaching stage, but a certain aliquot is sent to the wastewater treatment.

2.2. Operating Conditions

2.2.1. Characterization of PCBs

PCBs are manually dismantled, and specific components such as capacitors, heat sinks, transistors, and cables are removed. Hence, the PCBs are cut with shear in-pieces, with a size of around 2 × 3 cm. Sometimes, they may be additional physical treatments, such as gravimetric separations. Thus, the small pieces are milled by a knife mill equipped with a sieving mesh of 2 mm (Retsch SM2000, Haan, Germany). The ground material undergoes acid digestion according to the procedure detailed in Ippolito et al. [9], thus determining the concentration of the metals by inductively coupled plasma (ICP-OES, Agilent Technologies 5100, Santa Clara, CA, USA). Several mixed samples from PCs, mobile phones, and other devices have been characterized throughout the experimental activity, and the average composition and standard deviations are listed in Table 1.

2.2.2. Leaching Section

The operating conditions of the first leaching stages are the following:

- H_2SO_4: 1.8 mol/L;
- H_2O_2: 1.96 mol/L;
- pulp density: 15% wt/vol.;
- reaction time: 1.5 h;
- temperature: 25 °C;
- mixing speed: 250 rpm;
- mass of feed: 15 g.

Table 1. Composition of the PCBs used in the simulation.

Element	Concentration	Std Dev
Au	150 g/t	11 g/t
Ag	300 g/t	23 g/t
Cu	13.7% wt	0.4% wt
Al	4.6% wt	0.2% wt
Fe	4.9% wt	0.1% wt
Zn	4.7% wt	0.2% wt
Sn	2.3% wt	0.1% wt
Other metals	3.8% wt	-
Inert (plastics, resins, fiberglass, ceramic)	~66% wt	-

The reactions which take place are:

$$Cu + H_2SO_4 + H_2O_2 \rightarrow CuSO_4 + 2\,H_2O \tag{1}$$

$$Sn + H_2SO_4 + H_2O_2 \rightarrow SnSO_4 + 2\,H_2O \tag{2}$$

Copper has to be removed first, otherwise, it would consume thiourea in the second leaching, competing with gold. Instead, in the first step, the precious metals are not leached.

The first leaching stage works in a countercurrent operation mode, as shown in Figure 2. The pregnant solution from the second stage is recycled back into the first reactor in order to increase the concentration of the base metals of interest. Furthermore, this configuration results in a smaller volume of the spent solution generated at the end of the process and, hence, lower operating costs.

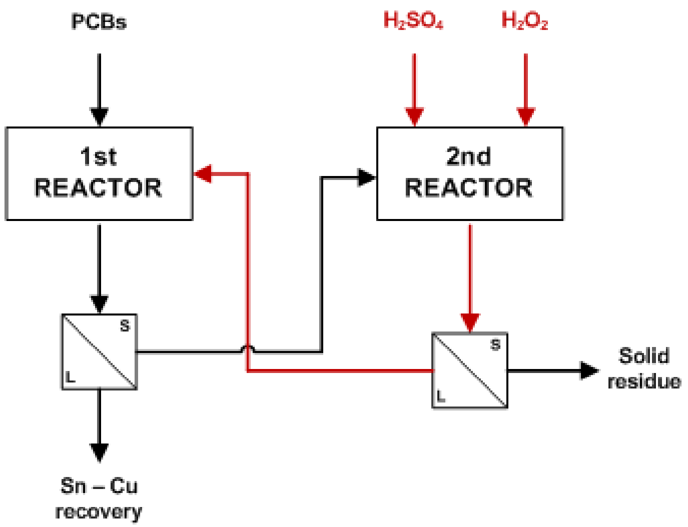

Figure 2. Countercurrent leaching in the first stage.

The concentration of copper is around 49 g/L as $CuSO_4$ (90% extraction yield in both reactors), whereas tin is nearly 5 g/L as $SnSO_4$ (80% and 50% extraction yields in the first and second reactors, respectively) after the countercurrent's first leaching stage.

After filtration, the PCBs undergo second leaching with different operating conditions:

- H_2SO_4: 0.2 mol/L;
- $Fe_2(SO_4)_3$: 22.5 g/L;
- $CS(NH_2)_2$–(thiourea): 20 g/L;
- pulp density: 10% wt/vol.;
- reaction time: 1 h;
- temperature: 25 °C;
- mixing speed: 250 rpm.

Fe^{3+} ions act as oxidant and thiourea as a complexing agent; sulfuric acid keeps the pH acidic, avoiding iron precipitation. The simplified reactions that involve precious metals are:

$$Au + Fe_2(SO_4)_3 + 4\,CS(NH_2)_2 \rightarrow [Au(CS(NH_2)_2)_2]_2SO_4 + 2\,FeSO_4 \quad (3)$$

$$Ag + Fe_2(SO_4)_3 + 6\,CS(NH_2)_2 \rightarrow [Ag(CS(NH_2)_2)_3]_2SO_4 + 2\,FeSO_4 \quad (4)$$

The mechanism of silver and gold extraction by thiourea in sulfuric medium containing Fe^{3+} ions leads to the oxidation of thiourea to formamidine disulfide [9]; the latter is unstable in acidic oxidative conditions and decomposes irreversibly to thiourea, cyanamide, and sulfur. Hence, if thiourea is not added in excess, such reagent will not be sufficient for the reactions reported in Equations (3) and (4) [31].

After the second stage, the concentration of the Au– and Ag–thiourea complexes is around 48 and 169 mg/L, respectively—the same concentrations of the pregnant solutions entering the related electrowinning processes. The extraction yield of the two precious metals is in the 85–90% range.

2.2.3. Recovery of Sn and Cu from Aqueous Solution

The pregnant solution from the first reactor undergoes tin precipitation by adding a cationic flocculant, i.e., polyamine, with a concentration of 2.5 mL/L of solution. The polyamine must be diluted with distilled water to a concentration of 10% *v*/*v*. The solution is slowly mixed at 50–100 rpm at room temperature for 30 min., a sufficient time to precipitate the metastannic acid, which is separated by filtration and dried at 100 °C for 2 h [32]. The precipitation yield is nearly 90%. The metastannic acid can be oxidized at 650 °C for 1 h to obtain high-grade tin oxide.

The solution resulting from filtration and containing copper sulfate undergoes electrowinning. The cathode is made of copper, whereas the anode is made up of titanium alloy. The current density is 250 A/m^2, voltage 1.5 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. The calculated energetic consumption is 2.1 kWh/kg, with a recovery of copper of around 98% and a current efficiency of 90%. Because of some contaminants, such as iron and zinc, energetic consumption is higher than typical values of about 1.5 kWh/kg range [34], but lower than identified by other studies in the case of contaminants [35].

2.2.4. Recovery of Au and Ag from Aqueous Solution

Au and Ag are recovered by two sequential electrowinning stages, with the following operating conditions:

- Gold anode:
  - titanium alloy;
  - cathode: graphite;
  - current density: 50 A/m^2;
  - cell voltage: 1.2 V;
  - time: 2 h;
  - temperature: 25 °C.
- Silver anode:
  - titanium alloy;
  - cathode: graphite;
  - current density: 75 A/m^2;
  - cell voltage: 1.4 V;
  - time: 2 h;
  - temperature: 25 °C.

The spent solution from the silver cell can be reused in the second leaching stage. The number of reusing cycles has to be determined, as other metal impurities such as Fe, Zn, and Ni tend to concentrate.

The recovery of Au and Ag by the electrodeposition is in the 85–95% range, and the energetic consumption is 4.1–4.4 kWh/kg per process. Unfortunately, the current efficiency is rather low, i.e., 15% for gold and 12% for silver. These efficiencies can certainly be improved with a higher concentration of the precious metals, which could be achieved by a countercurrent thiourea leaching stage or by processing PCBs with greater precious metal content.

2.3. Plant Description and Simulation

The entire process, tested on a lab-scale, was simulated in semi-industrial conditions by the software package SuperPro Designer v.9.5 (Intelligen Inc., Scotch Plains, NJ, USA). The capacity of the plant is 350 tons/year in a batch operating mode (2 tons/batch). Hence, the plant runs 175 days/year, considering one single batch per day. Nonetheless, this capacity could be fully industrial as the number of PCBs available on the market is not high, considering a thousand collectors are already sharing the market, primarily the black market, and that the breakeven capacity to make the investment profitable can be low. The feedstock composition used for simulation is the same as in Table 1.

The leaching section is composed of two stages: the first one, as aforementioned, is composed of two reactors (18 m^3 each) and the relevant plate and frame (P&F) filters in a countercurrent configuration. The volume of the reactor of the second stage is 19 m^3, whereas the P&F filter is equal to the previous two. Tin precipitation is carried out in a fourth reactor (18 m^3), but filtration is performed with a Nutsche filter, more efficient for metastannic acid, which is thus dried in a tray dryer.

The volume of the electrolytic cell for copper is 14 m^3. The pregnant solution from the second leaching stage undergoes electrodeposition of gold in another 12 m^3 electrolytic cell. Afterward, the spent solution is stored in a tank, whereas the operating parameters and cathodes are changed. Thus, the solution is transferred into the same cell for the electrodeposition of silver. The solid residue from the thiourea leaching stage is dried in a small belt dryer fueled with natural gas.

The plant is completed with storage tanks for reagents such as water, sodium hydroxide solution, sulfuric acid, and hydrogen peroxide, mixed tanks for storage of intermediate and treatment of waste solutions, pumps, grinder, mill, scrubber, some conveyor belts, etc. Solid reagents are stored in their original plastic bins or large bags.

The simulation was carried out using the operating conditions reported in the previous paragraph and the reaction yields obtained in the laboratory trials. The heat and mass balance of the entire plant and the economic analysis were carried out by Microsoft Excel, using data from SuperPro Designer v.9.5.

The economic analysis was developed according to Peters et al. [36]. It must be pointed out that the analysis is developed for a plant that does not consider the purchase cost of spent PCBs. Otherwise, purchasing PCBs represents another yearly operating cost that has to be considered in a recycling plant's economic valuation.

The minimum life of the plant was set at 15 years and the construction time at eight months, whereas the opportunity cost of the capital was set at 5%. The bank capital was considered to be paid back in 10 years and the interest rate of the loan was 3% [37,38]. The taxation level and the depreciation period were set at 25% and 10 years, respectively [36].

The following profitability indexes were calculated: net profit, return on investment (ROI), and payback time. Nevertheless, these indexes do not consider the money's time value. The discounted cash flow (DCF) analysis considers a project's cash flow and assesses the value of money over time. The indicators used for this analysis are the net present value (NPV), which measures the profit achieved by implementing the project. The profitability index (PI) measures the wealth achieved per unit of investment, and the discounted payback time (DPBT) quantifies the period of time the project needs to return from the initial investment cost. Aside from those indexes, the internal rate of return (IRR), which measures the project's economic return, is also provided.

3. Results

3.1. Economic Analysis

3.1.1. Capital Expenditure

The main equipment purchase cost is estimated using commercial offers from suppliers or estimating them from indirect methods indicated by Peters et al. [36]. The auxiliary and unlisted equipment includes a boiler, scrubber, compressor, pumps, cyclone, grinder, mill, belts, and storage tanks. The other items are estimated as a percentage of the equipment purchase cost and are proportional to the plant capacity and material treated. The total plant indirect cost (TPIC) items are also estimated as a percentage of the total plant direct cost (TPDC). Thus, the direct fixed capital (DFC) invested in this project is estimated to be EUR 3,516,958. Table 2 lists the detailed costs of the main equipment that have been estimated to determine the capital expenditure (CAPEX) reported in Table 3. Unlisted equipment was estimated as 30% of the purchase cost of the main equipment. It includes pumps, valves, grinder, mill, reagent storage tanks, dust abatement, scrubber, firefighting system, and one forklift.

Table 2. Evaluation of the main equipment purchase cost.

Equipment	Capacity	Cost (EUR)
Base metals leaching reactor (1)	17 m^3	55,000
Plate and frame filter	50 m^2	75,000
Base metals leaching reactor (2)	17 m^3	55,000
Plate and frame filter	50 m^2	75,000
Precious metals leaching reactor	19 m^3	58,000
Plate and frame filter	50 m^2	75,000
Electrolytic cell (copper)	-	350,000
Electrolytic cell (gold and silver)	-	350,000
Tin precipitation reactor	17 m^3	55,000
Nutsche filter	6 m^2	52,000
Tray dryer (SnO_2)	4 m^2	80,000
Belt dryer (leaching residue)	2 tons/day	170,000
Four storage tanks (plastics)	10 m^3	40,000

Table 3. Evaluation of CAPEX.

Item		Cost (EUR)
Main equipment		1,490,000
Auxiliary and unlisted equipment	30%	447,000
Drums/large bags for packaging		10,000
Laboratory equipment		250,000
Equipment Purchase Cost		**2,197,000**
Installation	12%	263,640
Piping	3%	65,910
Instrumentation	7.5%	164,775
Insulation	1.5%	32,955
Spare parts (2 years)	1%	21,970
Electricals	5%	109,850
Buildings	8%	175,760
Total Plant Direct Cost (TPDC)		**3,031,860**
Engineering, procurement, construction	10%	303,186
Supervision, start-up, and training	5%	151,593
Contingencies	1%	30,319
Total Plant Indirect Costs (TPIC)		**485,098**
Direct Fixed Capital (DFC)		**3,516,958**

3.1.2. Operating Expenditure

The operating expenditure (OPEX) is composed of several items listed in this paragraph. The reagents and raw materials required to carry out the process are reported in Table 4. The H and M balance is required to estimate the amount of reagents, product streams, energy consumption, and all the other running annual cost.

Table 4. Raw materials used in the recycling plant.

Raw Material	Consumption (Tons/Year)
Sulfuric acid (98% wt)	489
Hydrogen peroxide (30% vol)	202.7
Ferric sulfate (s)	37.1
Thiourea	26.3
Polyamine (l)	0.57
Water	677
NaOH(s)	2.80
CaO (s)	5.25
PCBs	350

The total water consumption is around 4183 tons/year, but around 3500 are recycled back into the process after the wastewater treatment or as spent solutions from the electrolytic cells. The rest is discharged into the sewage network to the industrial wastewater treatment plant (WWTP). Hence, the net consumption is 677 tons/year.

The total cost of raw materials is 218,400 EUR/year. Another important annual cost is due to utilities, mainly represented by electrical energy and natural gas. The electrical consumption is nearly 227,000 kWh/year for a total installed power of 208 kW. Hence, a power station of 215 kW is required for the plant. The two small dryers consume natural gas: the total consumption amounts to 51,794 EUR/year. Other utilities consist of technical and instrument compressed air produced on-site by one compressor.

The plant runs in batch mode, whose net duration is 10 h. The personnel comprises one technical director with administrative tasks, four skilled workers with maintenance duties, and a laboratory analyst for routine analysis and quality control. The annual cost is 248,430 EUR/year. The waste item accounts for the disposal of the PCB residue from the second stage leaching and some sludge and powder from the scrubber and dust filters. The wastewater treatment considers the cost of the treatment of the spent solution, carried out on-site, and the fee for discharging a small amount of treated water into the sewage network. Consumables include replacing cathodes and anodes consumed and other components such as gaskets, filters, lubricants, etc.

The greatest expense is the loan payment, which amounts to 343,351 EUR/year. The complete list of the operating costs is shown in Table 5.

3.1.3. Economic Evaluation Report

The economic evaluation summary is reported in Table 6. The revenues were calculated according to the current market prices, i.e., copper, tin, gold, and silver [39,40]. The plant produces 42.4 tons/year of copper, 7.2 tons/year of tin oxide, 43.8 kg/year of gold, and 85.8 kg/year of silver, all of which are commercial-grade metals. They are indicated in Figure 3.

Working capital is the investment in consumable materials, such as tied-up funds required to operate the business. It is composed of raw material, labor-dependent cost, waste disposal, and utilities, i.e., the minimum money to run the plant during the first year. The net profit was calculated as gross profit minus taxes plus depreciation [36]. The profitability indexes are calculated as follows:

$$Gross\ margin = \frac{Gross\ profit}{Revenues} \tag{5}$$

$$ROI = \frac{Net\ profit}{Total\ investment} \tag{6}$$

$$Payback\ time = \frac{Total\ investment}{Net\ profit} \tag{7}$$

Table 5. Evaluation of OPEX.

Item	Cost (EUR/Year)
Raw materials	218,400
Labor-dependent	248,430
Loan payment	343,351
Laboratory/QC/R&D	20,000
Consumables	60,000
Waste disposal	38,325
Wastewater treatment	42,061
Utilities (electric energy + methane)	51,794
Transportation	15,000
Miscellaneous	10,000
Running royalties	-
Maintenance and insurances	36,418
Annual operating costs	**1,083,779**

Table 6. Profitability summary.

Item		
Direct Fixed Capital	3,516,958	EUR
Working Capital	556,949	EUR
Start-up cost	15,000	EUR
Up-front R&D	10,000	EUR
Total Investment	4,098,907	EUR
Revenues	2,662,916	EUR/year
Annual Operating Costs	1,083,779	EUR/year
Gross Profit	1,579,136	EUR/year
Taxes	394,784	EUR/year
Net Profit	1,184,352	EUR/year
Gross Margin	59.3	%
ROI	28.9	%
Payback Time	3.5	Years

The gross margin is 59.3%, with a good return on the investment (ROI), amounting to 28.9%, and a payback time of 3.5 years. The overall project based on the recycling of PCBs is highly profitable.

Gross profit, ROI, and payback time are indexes that do not consider the time value of the money. Hence, the DCF analysis is also developed (detailed calculations are not reported here). To be conservative, an annual inflation rate of 1.5% is considered when calculating the operating costs; nevertheless, a 2% annual increase in the commodities price is also considered [41]. The depreciation period of a recycling plant is usually ten years [36].

The profitability index is 2.6 and is calculated as the ratio of the present value of the after-tax cash inflows to the present value of the cash outflows or capital items. This means that the business generates EUR 2.6 of profit for every euro invested in the project. The DPBT was also calculated and resulted in 2 years, i.e., the year in which the sum of the discounted cash flow becomes positive.

The IRR is the interest or discount rate for which the project's net present value (NPV) equals zero. In the present analysis, the IRR is around 150%. Moreover, the NPV is about EUR 10.7 M. Overall, this alternative analysis confirms the profitability of PCB recycling. Moreover, the indexes calculated above improve with the increase in the plant's capacity.

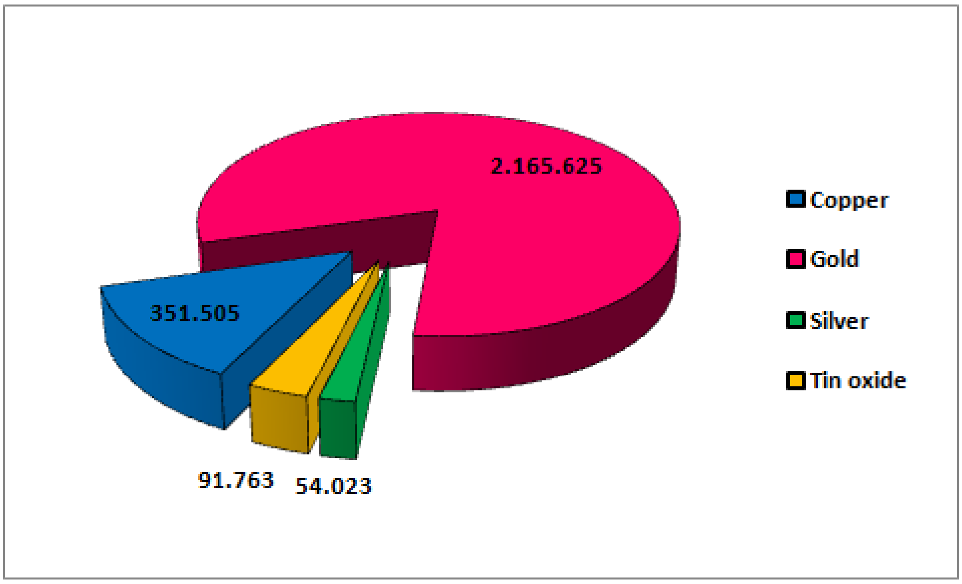

Figure 3. Annual revenues of the plant (EUR).

3.2. Sensitivity Analysis

The profitability analysis, as already mentioned, was carried out considering a null cost to collect the spent PCBs. Therefore, a sensitivity analysis was necessary to understand the upper value of the PCBs purchase cost corresponding to a profitable investment [1]. Hence, the calculation was also repeated for the cash flow analysis. Such indexes are all listed in Table 7.

Table 7. Summary of the profitability indexed varying the PCBs purchase cost.

PCBs Cost (EUR/Ton)	Gross Margin (%)	ROI (%)	PBT (Years)	NPV 5% (EUR)	IRR (%)	Profitability Index	Discounted PBT (Years)
0	59.3	28.9	3.5	11,228,042	158.8	2.74	2
500	45.6	21.3	4.7	7,985,581	100.9	1.87	3
1000	31.9	14.3	7.0	4,743,121	51.1	1.07	4
1500	18.2	7.9	12.7	1,500,661	16.4	0.32	5
2000	4.5	1.9	53.1	−1,741,799	−7.6	−0.36	>15

As it can be inferred from the table, with 1500 EUR/tons, economic values are still positive, albeit not as high as expected from a possible investor. Thus, the profitability limit of the process described in this paper can be set at 1000 EUR/tons.

We should consider that the PCBs are usually divided into three classes, depending on the content of gold: the first category includes those containing more precious metals such as gold and silver, namely those coming from PC's RAMs, microprocessors, and military devices, whereas the second category includes those less rich, such as PCBs coming from audio systems, cars, and liquid crystal displays.

4. Conclusions

This work analyzes the technoeconomic analysis of a PCB recycling plant—the most interesting WEEE in terms of metals and intrinsic economic value. The analysis was developed for a plant with a 350 tons/year capacity. The technical analysis was based on an industrial process based on lab-scale experimental results.

The modified Gold-REC 1 hydrometallurgical process includes a countercurrent first stage of leaching focused on copper and tin recovery, and a second stage of thiourea leaching to recover gold and silver. The extraction yield for the precious metals is in the range of 85–90%. Higher dissolution rates could be obtained by including a preliminary thermal treatment with the aim of removing organic compounds that can inhibit the oxidation of metals during the leaching operations. The tin is precipitated from the first leach liquor by adding a cationic flocculant with a yield of about 90%. Then, copper is recovered by electrowinning at 250 A/m^2 current density. Precious metals are recovered from the second leach liquor with sequential electrodeposition under different operative parameters. The spent solutions are recycled except for a purge sent to the wastewater treatment.

The profitability analyses, developed in case of no cost for collecting PCBs, demonstrated the overall advantage of investing in such a business. The DPBT is only 2 years, the NPV at 5% interest is EUR 10.7 M, and the profitability index is 2.6.

5. Patents

The patents resulting from the work reported in this manuscript are: "Process for the hydrometallurgical treatment of electronic boards. WO2018215967A1, Priority number IT201700057739 A (Gold-REC1) (2018)"; Hydrometallurgical Method for the Recovery of Base Metals and Precious Metals from a Waste Material. WO2019229632A1, Priority number-IT201800005826A (Gold-REC2) (2018).

Author Contributions: Conceptualization, N.M.I., F.F. and F.V.; methodology, N.M.I., F.F. and F.V.; software, G.P., N.M.I., F.F. and F.V.; validation, N.M.I., F.F. and F.V.; formal analysis, N.M.I. and F.F.; investigation, N.M.I., G.P. and M.P.; resources, F.V.; data curation, N.M.I. and F.F.; writing—original draft preparation, F.F.; writing—review and editing, N.M.I.; supervision, N.M.I., F.F. and F.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the European Commission under the Horizon 2020 program in the ambit of Treasure project (grant agreement N.101003587).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing not applicable.

Acknowledgments: The authors would like to acknowledge Lorenza Cichetti for her valuable contribution in the definition of a first simulation version of the Gold-REC 1 process as part of her bachelor's thesis.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Cucchiella, F.; D'Adamo, I.; Rosa, P.; Terzi, S. Automotive printed circuit boards recycling: An economic analysis. *J. Clean. Prod.* **2016**, *121*, 130–141. [CrossRef]
2. Jadhav, U.; Hocheng, H. Hydrometallurgical recovery of metals from large printed circuit board pieces. *Sci. Rep.* **2015**, *5*, 14574. [CrossRef] [PubMed]
3. Cui, H.; Anderson, C. Hydrometallurgical Treatment of Waste Printed Circuit Boards: Bromine Leaching. *Metals* **2020**, *10*, 462. [CrossRef]
4. Arshadi, M.; Yaghmaei, S.; Mousavi, S.M. Content evaluation of different waste PCBs to enhance basic metals recycling. *Resour. Conserv. Recycl.* **2018**, *139*, 298–306. [CrossRef]
5. Vakilchap, F.; Mousavi, S.M. Structural study and metal speciation assessments of waste PCBs and environmental implications: Outlooks for choosing efficient recycling routes. *Waste Manag.* **2022**, *151*, 181–194. [CrossRef] [PubMed]
6. Kumar, V.; Lee, J.C.; Jeong, J.; Jha, M.K.; Kim, B.S.; Singh, R. Recycling of printed circuit boards (PCBs) to generate enriched rare metal concentrate. *J. Ind. Eng. Chem.* **2015**, *21*, 805–813. [CrossRef]
7. Pinho, S.; Ferreira, M.; Almeida, M.F. A wet dismantling process for the recycling of computer printed circuit boards. *Resour. Conserv. Recycl.* **2018**, *132*, 71–76. [CrossRef]
8. Mir, S.; Dhawan, N. A comprehensive review on the recycling of discarded printed circuit boards for resource recovery. *Resour. Conserv. Recycl.* **2022**, *178*, 106027.
9. Ippolito, N.M.; Birloaga, I.P.; Ferella, F.; Centofanti, M.; Vegliò, F. Preliminary Study on Gold Recovery from High Grade E-Waste by Thiourea Leaching and Electrowinning. *Minerals* **2021**, *11*, 235. [CrossRef]
10. Havlik, T.; Orac, D.; Petranikova, M.; Miskufova, A. Hydrometallurgical treatment of used printed circuit boards after thermal treatment. *Waste Manag.* **2011**, *31*, 1542–1546. [CrossRef]

11. Birloaga, I.; Vegliò, F. Hydrometallurgical Method for the Recovery of Base Metals and Precious Metals from a Waste Material. WO2019229632A1. Priority Number-IT201800005826A (Gold-REC2) (2018). Available online: https://worldwide.espacenet.com/patent/search/family/063312319/publication/WO2019229632A1?q=pn%20any%20%22WO2019229632A1%22 (accessed on 16 February 2023).
12. Cui, J.; Zhang, L. Metallurgical recovery of metals from electronic waste: A review. *J. Hazard. Mater.* **2008**, *158*, 228–256. [CrossRef]
13. Sohaili, J.; Muniyandi, S.K.; Mohamad, S.S. A review on printed circuit boards waste recycling technologies and reuse of recovered nonmetallic materials. *Int. J. Sci. Eng. Res.* **2012**, *3*, 1–7.
14. Qiu, R.; Lin, M.; Ruan, J.; Fu, Y.; Hu, J.; Deng, M.; Tang, Y.; Qiu, R. Recovering full metallic resources from waste printed circuit boards: A refined review. *J. Clean. Prod.* **2020**, *244*, 118690. [CrossRef]
15. Wang, R.; Zhang, C.; Zhao, Y.; Zhou, Y.; Ma, E.; Bai, J.; Wang, J. Recycling gold from printed circuit boards gold-plated layer of waste mobile phones in "mild aqua regia" system. *J. Clean. Prod.* **2021**, *278*, 123597. [CrossRef]
16. Qiu, R.; Lin, M.; Qin, B.; Xu, Z.; Ruan, J. Environmental-friendly recovery of non-metallic resources from waste printed circuit boards: A review. *J. Clean. Prod.* **2021**, *279*, 123738.
17. Zhu, X.; Cui, T.; Li, B.; Nie, C.; Zhang, H.; Lyu, X.; Tao, Y.; Qiu, J.; Li, L.; Zhang, G. Metal recovery from waste printed circuit boards by flotation technology with non-ionic renewable collector. *J. Clean. Prod.* **2020**, *255*, 120289. [CrossRef]
18. Barnwal, A.; Dhawan, N. Recycling of discarded mobile printed circuit boards for extraction of gold and copper. *Sustain. Mater. Technol.* **2020**, *25*, e00164. [CrossRef]
19. Park, H.S.; Kim, Y.J. A novel process of extracting precious metals from waste printed circuit boards: Utilization of gold concentrate as a fluxing material. *J. Hazard. Mater.* **2019**, *365*, 659–664. [CrossRef]
20. Kumari, A.; Jha, M.K.; Lee, J.C.; Singh, R.P. Clean process for recovery of metals and recycling of acid from the leach liquor of PCBs. *J. Clean. Prod.* **2016**, *112*, 4826–4834. [CrossRef]
21. Dutta, D.; Panda, R.; Kumari, A.; Goel, S.; Jha, M.K. Sustainable recycling process for metals recovery from used printed circuit boards (PCBs). *Sustain. Mater. Technol.* **2018**, *17*, e00066. [CrossRef]
22. Gande, V.V.; Vats, S.; Bhatt, N.; Pushpavanam, S. Sequential recovery of metals from waste printed circuit boards using a zero-discharge hydrometallurgical process. *Clean. Eng. Technol.* **2021**, *4*, 100143. [CrossRef]
23. Bastin, F.; Janssen, A.; Lolivier, Y.; Masalskas, M.; Van Rechem, A.; D'Ans, P. Exploration of alternative routes for recycling critical metals from waste PCB and tantalum capacitors. *Procedia CIRP* **2020**, *90*, 437–442. [CrossRef]
24. Mairizal, A.Q.; Sembada, A.Y.; Tse, K.M.; Haque, N.; Rhamdhani, M.A. Techno-economic analysis of waste PCB recycling in Australia. *Resour. Conserv. Recycl.* **2022**, *190*, 106784. [CrossRef]
25. Deschênes, G.; Ghali, E. Leaching of gold from a chalcopyrite concentrate by thiourea. *Hydrometallurgy* **1988**, *20*, 179–202. [CrossRef]
26. Elena Poisot-Diaz, M.; Ignacio, G.; Gretchen, T.L. Electrodeposition of a silver-gold alloy (DORÉ) from thiourea solutions in the presence of other metallic ion impurities. *Hydrometallurgy* **2008**, *93*, 23–29. [CrossRef]
27. Urbanski, T.S.; Fornari, P.; Abbruzzese, C. Gold electrowinning from aqueous-alcoholic thiourea solutions. *Hydrometallurgy* **2000**, *55*, 137–152. [CrossRef]
28. Ubaldini, S.; Fornari, P.; Massidda, R.; Abbruzzese, C. An innovative thiourea gold leaching process. *Hydrometallurgy* **1998**, *48*, 113–124. [CrossRef]
29. Juarez, C.M.; Dutra, A.J.B. Gold electrowinning from thiourea solutions. *Miner. Eng.* **2000**, *13*, 1083–1096. [CrossRef]
30. Li, J.; Miller, J.D. A review of gold leaching in acid thiourea solutions. *Min. Proc. Ext. Met. Rev.* **2006**, *27*, 177–214. [CrossRef]
31. Cichetti, L. Analisi Di Processo per Il Recupero Di Metalli Preziosi da Raee Mediante Trattamenti Idrometallurgici. Master's Thesis, Università degli Studi de L'Aquila, L'Aquila, Italy, 2020.
32. Birloaga, I.P.; Ippolito, N.M.; Vegliò, F. A Mobile Pilot Plant for the Recovery of Precious and Critical Raw Materials. In *New Business Models for the Reuse of Secondary Resources from WEEEs The Fenix Project*; Chapter 5; Springer Briefs: Berlin/Heidelberg, Germany, 2021. [CrossRef]
33. Birloaga, I.P.; Vegliò, F.; De Michelis, I.; Ferella, F. Process for the Hydrometallurgical Treatment of Electronic Boards. WO2018215967A1. Priority Number IT201700057739 A (Gold-REC1) (2018). Available online: https://worldwide.espacenet.com/patent/search/family/060020492/publication/WO2018215967A1?q=pn%3DWO2018215967A1 (accessed on 16 February 2023).
34. Schlesinger, M.E.; King, M.J.; Sole, K.C.; Davenport, W.C. *Extractive Metallurgy of Copper*, 5th ed.; Elsevier: Edinburgh, UK, 2011; Chapter 17.
35. Da Silva, T.R.; Majuste, D.; Bauer, J.; Moats, M.S. Effect of zinc ions on copper electrodeposition in the context of metal recovery from waste printed circuit boards. *Hydrometallurgy* **2020**, *198*, 105513. [CrossRef]
36. Peters, M.S.; Timmerhaus, K.D.; West, R.E. *Plant Design and Economics for Chemical Engineers*, 5th ed.; Mc Graw-Hill: New York, NY, USA, 2004.
37. Cozza, G.; D'Adamo, I.; Rosa, P. Circular manufacturing ecosystems: Automotive printed circuit boards recycling as an enabler of the economic development. *Prod. Manuf. Res.* **2023**, *11*, 2182837. [CrossRef]
38. D'Adamo, I.; Ferella, F.; Gastaldi, M.; Ippolito, N.M.; Rosa, P. Circular solar: Evaluating the profitability of a photovoltaic panel recycling plant. *Waste Manag. Res.* **2023**. [CrossRef] [PubMed]
39. Kitco Metals. Available online: https://www.kitco.com/market/ (accessed on 16 January 2023).

40. London Metal Exchange. Available online: https://www.lme.com/Metals/Non-ferrous/LME-Tin#Trading+day+summary (accessed on 16 January 2023).
41. Ferella, F.; D'Adamo, I.; Leone, S.; Innocenzi, V.; De Michelis, I.; Vegliò, F. Spent FCC E-Cat: Towards a Circular Approach in the Oil Refining Industry. *Sustainability* **2019**, *11*, 113. [CrossRef]