Environmental Engineering and Management Journal

October 2024, Vol. 23, No. 10, 2029-2040
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2024.163

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AN INTEGRATED AND ECO-EFFICIENT PROCESS FOR MATTER RECOVERING BY WEEE RECYCLING: PINECOR PROJECT

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Abstract

The scarcity and supply difficulties of strategic elements for industrial ecosystems make the development of processes/technologies for their recovery from existing resources crucial. In this perspective, the recycling and collection of WEEE (Waste from Electrical and Electronic Equipment) are essential for the circular economy. In Italy, the e-waste stream is divided into two channels (domestic and professional) and five groupings. In 2023, 72% of the waste managed by recycling companies (around 367 ktons) came from the domestic sector, while 28% (around 144 ktons) came from the professional sector. From 2018 to 2023, the sequence of WEEE collected from the highest to the lowest is represented by groupings: R2 (Large Household Appliances), R1 (Cooling and Freezing Appliances), R4 (Consumer Equipment), R3 (Screen and Monitors) and R5 (Lighting equipment). R1, R2 and R4, which seem to represent the categories that would bring more environmental benefits (i.e., tons of CO_2 equivalent avoided) if properly processed and recycled, are the target secondary sources for the PINECOR project. The aim of such a project is to develop an integrated system, based on innovative, multifunctional and eco-efficient technologies for the recovery of glass, siliceous fraction, plastic and metal from WEEE. This paper presents the first results obtained in the project both in terms of separation processes developed to obtain high-purity recycled fractions, and in terms of techniques for the extraction and recovery of secondary raw materials, with particular attention to their application in the most common sectors and those in growth.

Key words: elutriation, glass, metals, plastics, secondary materials, separation procedures, WEEE

Received: May, 2024; Revised final: September, 2024; Accepted: October, 2024; Published in final edited form: October, 2024

1. Introduction

The amount of Waste of Electrical and Electronic Equipment (widely known as WEEE or e-waste) generated each year in the EU and around the world is increasing rapidly. With an annual growth rate of 2%, it is now one of the fastest growing waste streams (European Commission, 2020). It includes a wide range of equipment such as mobile phones, computers, televisions, refrigerators, household appliances, lamps, but also medical devices and photovoltaic panels (Chesmech et al., 2023; Khan et al., 2022). E-waste contains a complex mixture of materials, some of which are hazardous. This can cause major environmental and health problems if the discarded equipment's are not properly managed. Modern electronics also contain rare and expensive resources, including critical raw materials (Li, Co, Pt, etc.). At the end of its working life, Electrical and Electronic Equipment (EEE) must be recycled and

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therefore sorted into different groupings for collection. That is why WEEE is identified by the crossed-out wheeled bin symbol. All WEEE have specific tasks to perform to ensure the environmental sustainability of the system and thus contribute to the protection of the environment.

If managed effectively, this waste can be recycled and reused. In addition, improving the collection, treatment and recycling of the electronic equipment at the end of its life can increase resource efficiency and support the transition to a circular economy. It can also contribute to the security of supply of critical raw materials, ultimately strengthening the EU's strategic autonomy (Serpe et al., 2024).

In Italy, the collection and recycling of WEEE governed by Italian Legislative Decree 49/2014, which defines the direct liability of many different players: the producers of EEE, suppliers, local authorities and consumers. The Italian collection system divides the e-waste stream into two channels (domestic and professional) and five groupings. In 2023, the 72% of waste managed by the Recyclers (about 367 ktons) came from the domestic sector, while 28% (about 144 ktons) came from the professional sector. From 2018 to 2023, the sequence of WEEE collected from the highest to the lowest is represented by groupings: R2 (large household appliances), R1 (cooling and freezing appliances), R4 (consumer equipment), R3 (screens and monitors) and R5 (lighting equipment) (CDC RAEE, 2018 2019, 2020, 2021, 2022, 2023a, 2023b).

As mentioned above, WEEE is a problem, but also a great opportunity to recover very valuable fractions and therefore the collection, management and recycling phases are strategic. The target of a minimum collection rate of 65% for WEEE is an ambitious goal for European countries due to the lack of skills, scarcity of effective technologies and gaps in the collection phase. Furthermore, according to the European Commission, the design of products determines up to 80% of the environmental impact of their life cycle: most of the products currently placed on the market are designed without taking into account, or insufficiently taking into account, their recyclability and the end-of-life phase (European Commission, 2024).

With almost one million tons/year of electrical and electronic equipment entering the Italian market (continuously growing), just over 350,000 tons/year of WEEE are separately collected, or 40% (5.8 kg/inhabitant) compared to a European target of 65% (9.8 kg/inhabitant). These quantities are recycled at a rate of 89% (EERP R, 2024).

There is undoubtedly a gap at the collection phase, largely due to the behaviour of citizens who do not manage end-of-life properly. However, it should be borne in mind that, at present, some fractions of separate collection are exported to other European countries, due to the lack of dimensional and technological facilities, and that in the coming years we will have to increase separate collection by at least 200,000 tons/year (EERPR, 2024).

There is a clear need for financial support for the construction of the plant infrastructure required to take advantage of this industrial opportunity. In order to improve waste management and the circular economy, to strengthen the infrastructures for separate collection, to modernize or build new waste treatment plants, and to bridge the gap between the regions of the North and those of the Center-South (today about 1.3 million tons of waste are treated outside the region of origin), important financial support policies have been implemented in Italy. One of them is the National Resilience and Resistance Plan (NRRP), established by the Government in 2021 with Legislative Decree no.59. The funds earmarked for the private sector in the waste cycle, identified by Investment Line 1.2 "Lighthouse projects for the circular economy", have been allocated to innovative projects for the treatment and recycling of waste from the four strategic supply chains identified by the Circular Economy Action Plan promoted by the EU, namely: Plastics, Paper and cardboard, WEEE (including photovoltaic panels and wind turbines) and Textiles. The total amount of investment has been divided into four equal parts, i.e. 150 million euros for each line of intervention. The objective of these interventions is to support the achievement of recycling targets in the sectors identified by in the Circular Economy Action Plan for each supply chain financed by the NRRP. In particular, the targets set in Italy for WEEE are 55% recycling (AssoAmbiente, 2023). In terms of financial resources dedicated to research and innovation projects, the most important action is the one led by the Italian Ministry of the Environment and Energy Security (MEES) with the Call for co-financing of WEEE Research Projects, approved in 2020 by the Ministerial Decree of the Ministry of the Environment of 9 December 2020, prot. n. 74, with a budget of 900,000 euros. The 2020 edition of this Call also includes the PINECOR project.

In most WEEE treatment facilities, after sorting and pre-treatment (usually mechanical), processing intermediates are obtained that are not market-ready: to become end-of-waste/products they require further purification and separation processes. Often these processes are not only complex, energy-intensive and focused on quantitative rather than qualitative yields, but are also specialized in only one type of "key- fraction" or "valuable fractions" (e.g. the process for recovering recycled plastic is different from that for recovering base metals). In this context, PINECOR aims to provide a multifunctional solution, capable of working as an integrated process to recover glass, siliceous fraction, metal and plastic simultaneously. In fact, despite the type of treatment and the recyclable materials and residual fractions, which vary according to the grouping treated, PINECOR is a flexible and adaptable process capable of efficiently treating three different groupings of

WEEE (R1, R2, R4) with the highest Italian collection rate.

2. Materials and methods

2.1. PINECOR project: context, process and materials

PINECOR (*ECO-efficient and Integrated Process for WEEE Recovery)* is an Italian research project co-funded by the Ministry of the Environment and Energy Security ("Ministero dell'Ambiente e della Sicurezza Energetica" - MASE), which aims to develop a **P**rocess based on an **IN**tegrated and **ECO**-efficient system capable of covering the entire WEEE **R**ecycling value chain, from the identification and collection of WEEE (and/or its target components) and the associated pre-treatment processes, separation, purification and recovery processes, to industrial applications through the creation of prototypes. Based on innovative, multifunctional and eco-efficient technologies, the main objective for the PINECOR process is the recovery of the glass, siliceous fraction, plastics and metals from WEEE.

PINECOR focuses on the recovery of secondary raw materials from specific groupings of WEEE: R1, R2, R4. Forsmall household appliances (R4), two processes have been tested for the separation of the product fractions (mainly metals and plastics): different types of dense homogeneous liquids and elutriation equipment.

The recovery of Cu through a chemical process of leaching and galvanic electrodeposition was also studied, using the same chemical solution for both phases. With regards to categories R1 and R2 the work focused on the recovery of glass from refrigerator shelves and washing machine portholes, introduced in the formulation of frits for ceramic glazes and in ceramic supports, with parameters comparable to standard formulations.

The collected and selected WEEE will be treated using an integrated approach, with innovative multifunctional eco-efficient technologies, for glass, plastic and metal recovery. To "close the loop", promising value chains will be developed through a qualitative study of eco-sustainable applications in specific industrial sectors, from the most common (i.e. ceramics, construction etc.) to those in expansion (e.g., green building). Groupings R1, R2 and R4 represent the growth drivers of annual e-waste collection volumes at national level (Table 1).

Last year, there was a decline in grouping R3 – TV sets and monitors which, after the exponential growth in 2021 and 2022 linked to the TV bonus, continued in the physiological downward trend and recorded a significant decline in 2023. Contrary to the trend for category R3, all the other four groupings show a positive growth instead. R1, R2, R4 could represent, within the WEEE groupings, the categories that would bring more environmental benefits (i.e., tonnes of CO_2 equivalent avoided) if properly processed and recycled: up to 1.64 tons of CO_2 equivalent avoided by the proper recycling of the R4 grouping, 1.40 tons for R1, followed by 1.05 tons for R2 (Remedia and IEFE-Bocconi University, 2017).

The WEEE pre-treatment stages within PINECOR are shown in Fig. 1: the input stream was sent to specific pre-treatment lines for WEEE grouping; the first phase was manual dismantling to extract the main components and sorting to separate and store the hazardous components, then the main components were sent to coarse grinding (up to 4 cm) to obtain the target fractions for the recovery processes. Five fractions, organized into samples, were obtained from the WEEE pre-treatment process carried out in the operating sites of the project partner *Treee*, according to their already standardized procedures.

The R1 and R2 streams glass from refrigerator shelves *TRE_PIN01* and washing machine portholes *TRE_PIN02*. A heterogeneous yielded mixture constituting mainly of plastics and metals, called *TRE_PIN03,* was extracted from small household appliances from grouping R4. Finally, after manual dismantling, shredding, magnetic separation and sieving of end-of-life photovoltaic panels (belonging to grouping R4), two fractions were obtained: *TRE_PIN04-BATCHA,* consisting mainly of plastics, glass fragments and metal residues, and *TRE_PIN04-BATCHB,* consisting mainly of glass from end-of-life photovoltaic panels. All these materials were then subjected to additional optimization processes of size reduction (0 - 0.5 mm for the glasses and 0 - 1 mm for the mixture by small household appliances) carried out by an external company in order to better prepare the outputs of the pre-treatment for the subsequent separation/valorisation steps.

Table 1. Percentage of WEEE collected from 2018 to 2023 per group and average weight of the total amount (source Annual Reports by CDC RAEE)

WEEE Groups	*2018 (%)*	*2019 (%)*	*2020 (%)*	*2021 (%)*	*2022 (%)*	*2023 (%)*	*Average values*
R1	27.1	27.2	26.5	25.9	27.4	28.9	**27.2**
R2	32.8	33.6	34.3	33.6	32.5	34.9	**33.6**
R3	19.2	17.4	17.0	19.8	19.7	13.8	**17.8**
R4	20.3	21.2	21.4	20.1	19.8	21.9	**20.8**
R5	0.6	0.6	0.7	0.7	0.7	0.5	**0.6**
tot	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**

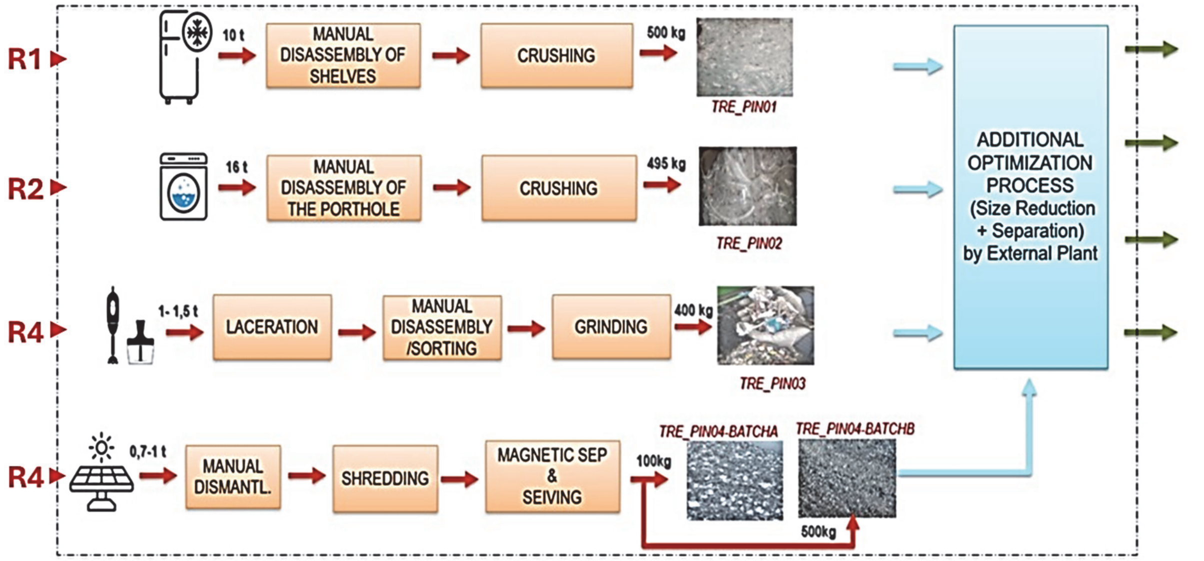


Fig. 1. Pre-treatment of WEEE target stream in PINECOR

2.2. Pinecor methods: separation and extraction process

Given to the heterogeneous nature of the starting material from *TRE_PIN03*, it was first necessary to develop a process for separating metal and plastic, using two approaches.

Firstly, a well-known separation method, the use of homogeneous dense liquids, which is now used in other fields, was adopted and adapted to this specific need to separate the two different fractions mentioned above. First of all, the real densities of the different plastics that made up the sample under investigation, as well as the densities of the metal fractions, were researched in the literature. It is obvious that the density of the latter was significantly higher than that of the plastics. Following the same principle, the densities of the most common saline solutions - potassium carbonate, soda, etc. - were researched in the literature until a saline solution was found with a density between that of the heaviest plastic and the lightest metal. Using the chosen saline solution, the metals (from the lightest to the heaviest) tended to sink during the application of this method, while the plastics (from the heaviest to the lightest) tended to float, allowing them to be separated. The solutions selected and tested were: NaOH 30% (density 1.31 g/cm^3), NaOH 50% (density 1.50 g/cm^3), K_2CO_3 50% (density 1.54 g/cm^3), $ZnCl_2$ 70% (density 1.88 g/cm^3). Five g of *TRE_PIN03* are added to a beaker containing 200 g of each of the above solutions , the sample is for approximately 15 minutes using a mechanical stirrer and once the stirring is stopped, the separation obtained (metal on the bottom and plastic on the top) can be observed.

The second method tested, more performing, is separation by elutriation (Fig. 2). The laboratory apparatus (elutriator) separates the different particles of the sample according to their size, shape and density, using a flow of water in the opposite direction to that of sedimentation. The elutriator is equipped with a hole at the bottom for the introduction of the water flow and 3 holes placed at different heights to separate materials with different specific weights (Fig. 2a). A constant flow of water is introduced from the bottom of the apparatus and the material is separated into four fractions according to its density. In detail, the experiment takes place in several steps: initially, the first hole from the top is used, from which the material with the lower density comes out, then the other two holes are used, from which material with a prograssively higher density comes out. Finally, the material remaining at the bottom is the one with the highest density. The material is first weighed, then moistened with denatured ethyl alcohol to increase its wettability, and then fed into the machine. Smaller or lighter particles are carried to the top and higher density particles remain at the bottom and are then extracted. In the end, 4 samples are obtained, which are then characterized.

Plastics are dried and characterized by FT-IR, DSC and Melt Flow Index (MFI), and metals by Inductively Coupled Plasma (ICP). DSC and FT-IR are the most commonly used identification techniques for polymeric materials. DSC is mainly used for semi-crystalline materials because the melting point is visible, IR is used for all polymers, but in this case it is necessary to identify any amorphous ones and to integrate the results of the two techniques. As for FT-IR, 5 polymer particles per color extracted from each sample were analyzed in order to identify the different polymers constiuents of the mixtures. As for DSC and MFI the mixtures coming from the three holes of the elutriator were ground in order to obtain a homogeneous material. Five replicates were carrie out for each mixture.

One of the main objectives was to recover the metal fraction separated by elutriation (as an unseparated bottom body), following a process of chemical leaching and galvanic electrodeposition using the same solution consisting of hydrochloric acid (HCl) and copper chloride ($CuCl_2$). The recovery of Cu took place in two steps: 1) Chemical leaching in an acidic environment: ca. 0.5 g of the *TRE_PIN03* metal fraction is placed in a 100 mL beaker together with about 50 mL of leaching solution. The beaker is placed on a magnetic stirrer with a heating table. The sample is kept stirred at a temperature of about 50°C, for a variable time; 2) Galvanostatic electrodeposition of Cu was carried out using an electrochemical cell with three electrodes: copper working electrode (WE); platinum counter electrode (CE); Silver – Silver Chloride, SSCE (Ag / AgCl / KClsat), reference electrode (RE). In particular, two electrochemical cell designs were tested (Fig. 3a-b). The copper working electrodes were analyzed by SEM-EDS to evaluate the composition and morphology of the electrodeposited metal. The aim of the final phase of the experiment was to recover the siliceous phase by treating the ground glass fractions belonging to the groupings R1 (glass from refrigerator shelves), R2 (glass from washing machine portholes), and R4 (glass from photovoltaic panels) with a technology that would help to reduce energy costs. For these reasons, in order to extract the siliceous fraction from the selected target materials, a semi-industrial scale pilot plant has been used, which includes a reactor in which intense cavitation is applied to the reactive mass.

The innovation of this reactor lies in the fact that cavitation is generated by the rotation of a rotor with an ad hoc geometry inside a specific rotor. In this apparatus, there are no piezometric or magnetostrictive transducers, bringing advantages in terms of equipment simplification. The modulation of the cavitation intensity is achieved by varying the rotor speed and the operating pressure. This apparatus allows for the activation of the glass dissolution reaction in an alkaline medium starting from 50°C.

The system designed and implemented as a pilot plant (Fig. 4) consists of:

(a) (b) (c)

Fig. 2. Elutriator: (a) schematic representation; (b) before the separation test; (c) separated metal fraction on the bottom at the end of separation test

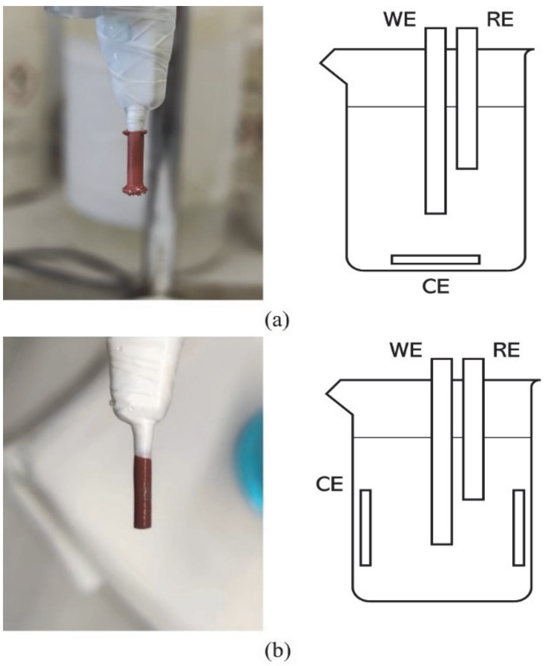


Fig. 3. First (a) and second (b) electrochemical cell configuration

- A thermostatic reactor with associated auxiliary circuit for temperature maintenance and a mixer to prevent sedimentation of the solid fraction during the process;
- Piping and pumping system for solution recirculation;
- Shock Power Reactor (SPR) cavitation system;
- Automatic control and command system via Siemens PLC.

Fig. 4. Pilot Plant for the recovery of the siliceous phase

The plant is equipped with sampling ports and can be operated in semi-automatic or fully manual mode. The main parameters considered during the test set-up phase were:

1. Type of glassy matrix and its composition;
2. Mass ratio: glassy matrix/water/NaOH in the reacting mixture;
3. Temperature inside the reactor;
4. Pressure in the recirculation circuit;
5. Residence time in the cavitation chamber;
6. Rotation speed of the SPR.

The tests were carried out by sequentially loading the liquid fraction (water + NaOH in the chosen proportions) into the reactor, and after starting the plant, the solid fraction was introduced. It was decided to progressively introduce small quantities of glass to allow the system to circulate the suspension gradually, in order to mitigate the high abrasive capacity of this type of matrix on surfaces (including AISI316 steel). This phenomenon is accentuated inside the SPR reactor.

3. Results and discussion

3.1. Separation and extraction process results

Figure 5 shows the results of the separation of the metal and polymer fractions of small household appliances of sample *TRE_PIN03* by dense homogeneous liquids, namely NaOH 30% (density 1.31 g/cm^3), NaOH 50% (density 1.5 g/cm^3), K_2CO_3 50% (density 1.54 g/cm^3) and $ZnCl_2$ 70% (density 1.9 g/cm^3). $ZnCl_2$ gave the best result due to its higher density: copper wires are deposited at the bottom, the polymer fraction appears at the surface and there is no material in the middle. This method was not applied to R4 photovoltaic panels.

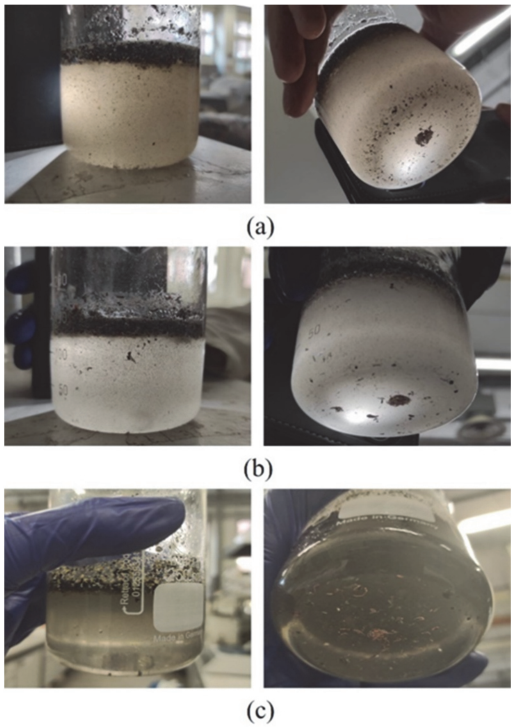


Fig. 5. *TRE_PIN03* size 1 mm (5 g) in 200 g of:
(a) NaOH 30%; (b) NaOH 50%; (c) $ZnCl_2$ 70%

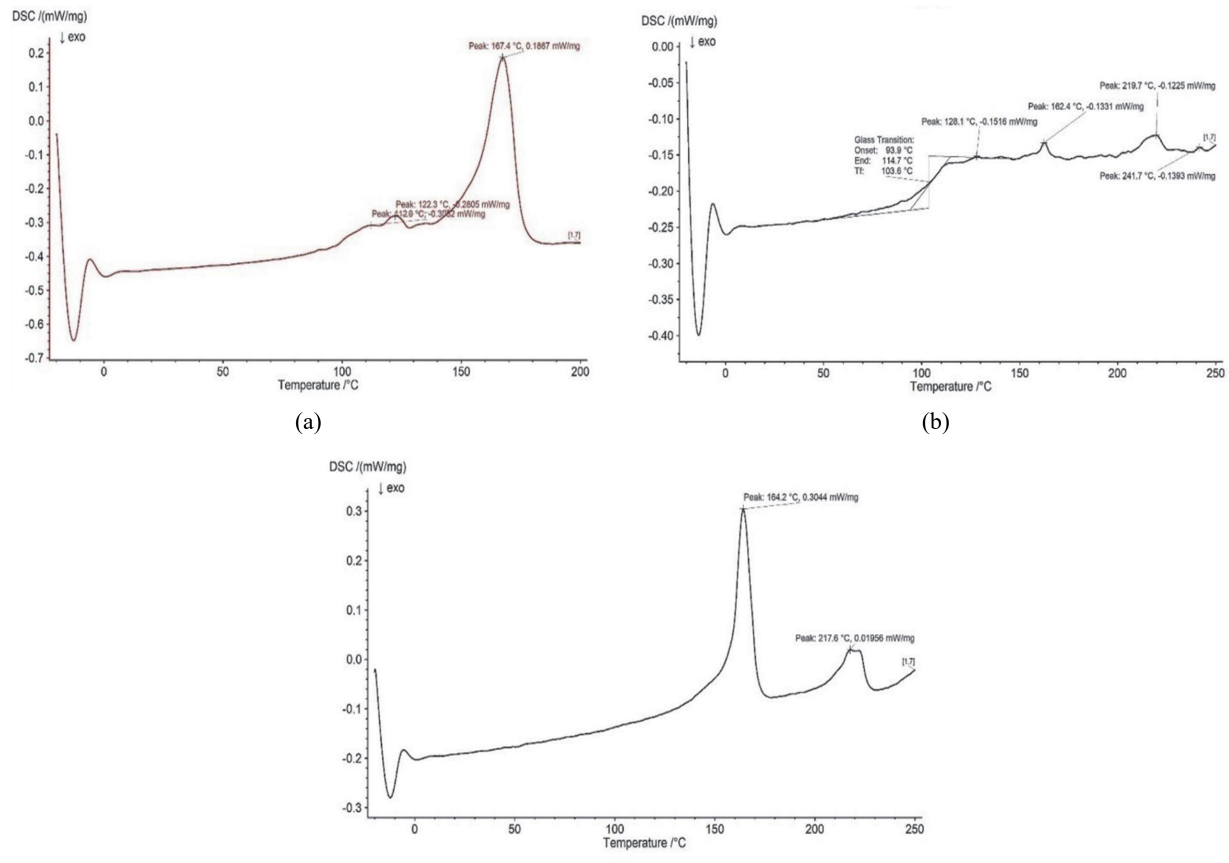
Table 2 shows the chemical composition of the metals recovered from the elutriation process, which allowed the separation of 28% of light plastics (such as polypropylene), 34% intermediate plastics (such as ABS), 10% heavy plastics (such as polycarbonate) and 4% mainly metals, with an in-process material loss of 24%. The percentages were calculated on the basis of the incoming sample weight. The most abundant metal is Cu followed by Fe, Pb, Sn and Al.

As regards plastic fractions obtained by elutriation, DSC analysis (Fig. 6), FT-IR analysis and MFI values are reported (Table 3). The DSC melting peaks identified are at 112 and 122°C corresponding to LDPE and HDPE; at 167°C associated with polypropylene (Fig. 6a). The Tg (glass transition) can be attributed to both polystyrene, and some blends such as SAN (styrene-acrylonitrile) and ABS (acrylonitrile-butadiene-styrene). In Fig. 6b polypropylene (melting peak at 162°C), PA6 polyamide (melting peak at 219°C) and ABS (Tg at 103.6°C) are identified. In Fig. 6c, the melting peak (164°C) is attributable to polypropylene or polyoxymethylene (acetal) (POM), while that at 217°C to PA6. The results of the thermal analysis are compatible and correlated with the MFI values. The MFI values range from about 3g/10min (high viscosity) to about 15 g/10min (low viscosity) (Table

3). The MFI value implies different processing conditions of the polymer, therefore the MFI values can be used to identify the technology of use of the material and provide information on heterogeneous polymeric masses. Low MFI values favour the use of extrusion technology, while high MFI values favour injection molding. The MFI is also an indirect qualitative measure of the molecular weight of the polymer and is also dependent on the degradation of the material. As the thermal degradation of the polymer increases, an increase in the MFI is also observed (due to the decrease in the molecular weight and therefore in the viscosity). In this case, the MFI values obtained identify a molded material that can be remolded. The FT-IR analysis was carried out on 5 different polymer particles chosen based on their color. Table 3 summarises the different polymers identified in the three fractions obtained from the elutriation process.

Table 2. ICP Chemical analysis of the metal fraction at the bottom of the elutriator from *TRE_PIN03* sample

Metal	*Concentration [mg/kg]*
Cu	560.183
Al	8.008
Pb	22.232
Ag	2
Au	< 12.5
Sn	15.006
Fe	82.897



(a) (b) (c)

Fig. 6. DSC analysis: (a) light weight fraction (hole 1) of polymers separated through elutriation process; (b) medium weight fraction (hole 2) of polymers separated through elutriation process; (c) heavy weight fraction (hole 3) of polymers separated through elutriation process

Table 3. Main polymers found per hole according to the FT-IR Analysis and MFI values measured on the fractions

Hole 1 – lightweight plastic ****MFI 15.3g/10min***	***Hole 2 – medium weight plastic*** ****MFI 7.5g/10min***	***Hole 3 – heavy plastic*** ****MFI 3.2g/10min***
Polystyrene (density about 1.050 g/cm^3)	Polypropylene (PP) (density about 0.855 g/cm^3 - 0.946 g/cm^3)	Polycarbonate (PC) (density about 1.200–1.220 g/cm^3)
Polypropylene (PP) (density about 0.855 g/cm^3 - 0.946 g/cm^3)	Acrylonitrile butadiene styrene (ABS) (density about 1.060–1.080 g/cm^3)	Polyoxymethylene (acetal) (POM) (density about 1.410–1.420 g/cm^3)
Styrene acrylonitrile (SAN) (density about 1.080 g/cm^3) Low-density polyethene LDPE (density about 0.94 g/cm^3) High-density polyethene HDPE (density about 0.96 g/cm^3)	High-density polyethene HDPE (density about 0.96 g/cm^3)	Polyamide (PA 6) (density about 1.120 g/cm^3 – 1.500 g/cm^3)

Regarding the copper recovery, careful work was carried out to optimize the etching and deposition parameters in order to obtain a controlled morphology and composition of the deposited copper. In particular, the second electrochemical cell configuration tested made it possible to obtain a more homogeneous and smooth morphology (compare Fig. 3 a-b). The optimization of the concentration of the leaching solution and electroplating current density allowed to obtain the deposition of pure copper without chlorine contamination with a high faradaic yield (45%). The absence of chlorine in the deposit is an important result considering the high concentration of chloride ions, which strongly complex the copper ions in the leachate. The optimization work made it possible to achieve the rate of 50 mg/h for leaching and 10 mg/h for galvanic electrodeposition with homogeneous morphology. The results of the SEM-EDS (micrography and chemical semi-quantitative analysis) are shown in Fig. 7.

For the extraction of the siliceous fraction from the glasses of refrigerator shelves *TRE_PIN01*, washing machine portholes *TRE_PIN02*, and photovoltaic panels *TRE_PIN04-BATCHB*, the effects of different parameters on the process outcome were analyzed:

- Glass matrices: no different reactivity is observed depending on the type of glass fraction treated;
- Effect of the glass matrix/water/NaOH mass ratio in the reaction mixture: the role of water is mainly to facilitate the transport of the mixture, while the minimum amount of NaOH to activate the process is around 20% by weight. The optimum mass ratio of glass to reaction liquid is approximately 1:2;
- Effect of temperature: tested temperatures ranged from 25°C to 65°C. This variation does not significantly affect the reaction yields, indicating that temperature is not the critical process parameter;
- Effect of pressure in the recirculation circuit: the effect of pressure was tested with a variation between 2.5 bar/6 bar, with slight evidence of increased yield with increasing pressure;
- Effect of the residence time in the cavitation chamber: the experimental data obtained show that the reaction initiation is rapid (a few seconds of contact in the cavitation chamber are sufficient for initiation) and that the maximum glass solubilization state is quickly reached. Once this concentration limit is reached, the residence time becomes irrelevant for further increase;

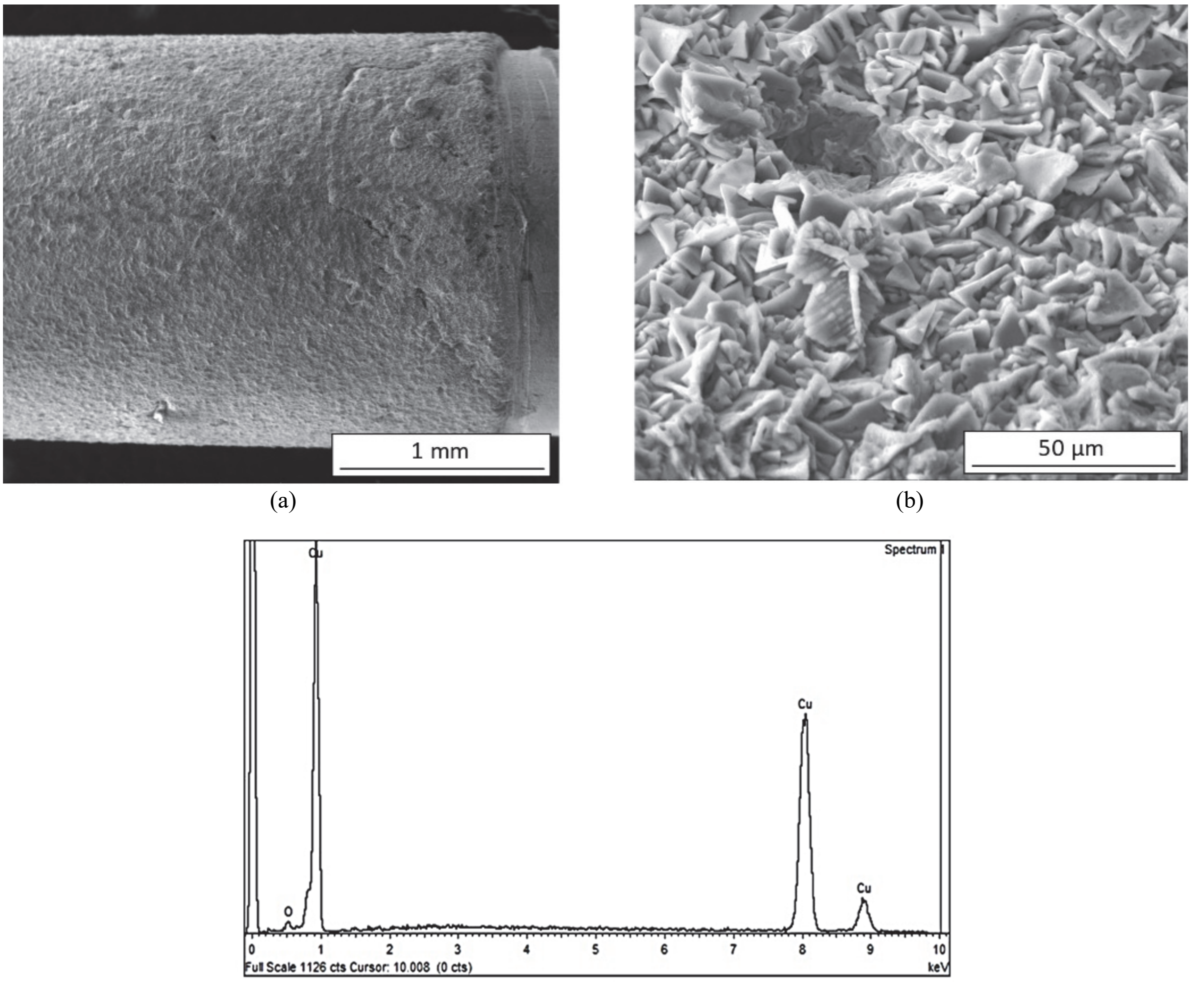


Fig. 7. SEM-EDS results: (a) and (b) Micrographs at different magnification of electrodes subjected to galvanic copper plating in a direct current procedure; (c) EDS spectrum of the electrode subjected to direct current eletroplating

- Effect of the SPR rotation speed: both the ignition speed and the reaction yield depend on the speed of the cavitation rotor. Below 3000 revolutions per minute, rpm, the reaction does not take place.

During the pilot plant phase, various semi-quantitative analytical routes were also tested to speed up the identification of the sodium silicate fraction in the solution. In addition, the experiment is verified that the reaction appears to be "blocked" after an initial glass solubilisation phase. It was found that the soluble glass fraction increases over time without the application of any thermal or mechanical stimulation.

This seemingly inexplicable phenomenon is explained by interpreting the mechanism of glass dissolution in sodium hydroxide solution. Glass is a polymeric structure obtained from the reaction of silica, boric anhydride, and alumina with alkali and alkaline earth metal oxides at a temperature of at least 1350°C. Attack of this structure by sodium hydroxide progressively removes the $(SiO_3)^{2-}$ anion to form soluble silicate. The remaining solid polymeric structure becomes unbalanced and attempts to rearrange itself by expelling more silica and forming new bonds with the ions present. The system operates at a low temperature, around 50°C, which makes the rearrangement kinetics very slow. In any case, glass treatment with NaOH in the SPR reactor is worthwhile, even though all the process parameters still need to be optimized. The "standard" treatment of glass with NaOH to obtain soluble silicates is carried out at a minimum temperature of 220°C with a minimum contact time of 2 hours at a pressure of 25 bar. This treatment is carried out in internationally industrialized processes. The reaction results in a mass composed of: a water-soluble liquid fraction, an intermediate fraction of gelatinous consistency and a solid fraction composed mainly of a white compound with residues of unreacted glass.

Finally, sodium silicate is present in the soluble fraction obtained from the glass treatment. Its presence and quantity have been indirectly verified by precipitation through hot treatment in the presence of a safe excess of sulfuric acid. Sodium silicate is converted into silica and sodium sulphate. Any other cations present, bound to the silicate anion, are also converted to sulphates. Washing removes salts from the silica. Precipitated silica was analysed by SEM-EDS before and after the S removal purification process (Table 4). The unpurified silica precipitate contains S residues derived from sulfuric acid (Fig. 8). The analysis shows the successful removal of S by washing and the prevalence of SiO_2.

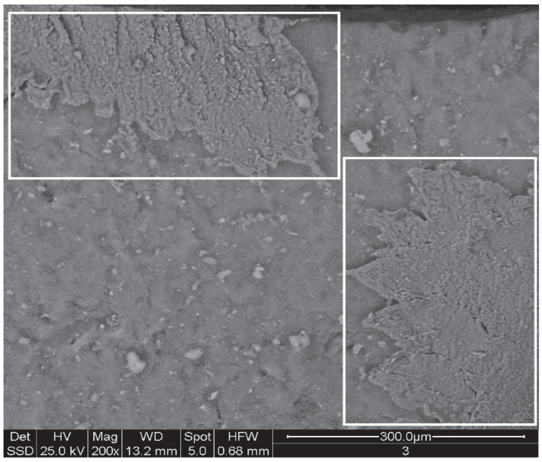


Fig. 8. Micrographs acquired by ESEM scanning electron microscope of precipitated silica before purification. The highlighted areas at the top left and bottom right are rich in S (approx. 22 weight%), the remaining area contains trace amounts of S (approx. 2 weight%)

3.2. Applications in ceramic sector of glass fractions

One of the most promising sectors for glass recovery is the ceramics sector. In fact, the sales of tiles in Italy in 2022 are estimated at 458 million square meters and this important market may incorporate a large amount of WEEE glass (Endhoven, 2023). In order to better address the research on the use of glass in the ceramic sector (both glaze and support), *TRE_PIN01* and *TRE_PIN02* were characterized by chemical (XRF and ICP), thermal (DTA and heating microscope), thermomechanical (Dilatometry) and mineralogical (XRD) point of view.

Table 5 shows the chemical composition of the glasses and Table 6 summarizes the characteristic temperatures and the expansion coefficients (EC) of the glasses that were identified by DTA, heating microscope and dilatometric analysis. From the chemical analysis it is clear that the refrigerator shelf glass (*TRE_PIN01*) is richer in alkaline earth metal oxides than the washing machine portholes glass (*TRE_PIN02*) and both glasses have a low content of chromophore components. Moreover, sample *TRE_PIN02* contains a small amount of B_2O_3.

Table 4. SEM-EDS Chemical analysis of precipitated silica from washing machine portholes *TRE_PIN02* glass pre and post purification

	Precipitated silica before purification	***Precipitated silica after purification***
Element	Weight%	Weight%
O	46.97	59.57
Na	22.36	2.44
Al	0.32	1.08
Si	11.39	36.60
S	18.96	0.31
Totals	100.00	100.00

DTA analysis show that the two glasses have similar thermal behavior, they are stable glasses that do not crystallize (absence of exothermic phenomena). XRD analysis shows that the two glasses are completely amorphous, with no crystalline phases present.

The research was based on replacing a percentage of the atomized mixture with WEEE glass, rather than replacing a single raw material in the mixture. This is a valid solution especially for factories that do not have a complete ceramic cycle, but start directly from the atomized product prepared by third parties. The percentages of substitution tested were: 2.5%, 5%, 10%, 15%, 20% respect to the solid content. In particular, the study discusses the results on the sintering process (total porosity) and on the technological properties (WA%, LS%).

The products obtained were characterized and compared with the standard (atomized without replacement) to verify the variability of the physico-mechanical properties and the applicability of the processes (Table 7). The tests were carried out on samples prepared by tile-making process on a laboratory scale, but the firing was performed in a ceramic roller kiln with the industrial cycle (1200°C, 48 min). The effect of the amount of WEEE glasses into the porcelain stoneware body does not affect the WA%, in fact there are no significant variations with respect to the reference (standard support) and in any case all the compositions are below the 0.5% limit corresponding to highly sintered ceramic tiles (Group BIa).

As for the linear shrinkage, it increases by about 2.6% in the composition with *TRE_PIN01* glass (15 wt%) and 11% with *TRE_PIN02* glass up to 10 wt%, then it drops to values lower than the standard, indicating a decrease in densification, certainly due to an increase in the glassy phase present. The effect on porosity is positive up to 10 wt% of inserted glass for all two glass-based samples. Mechanical tests were carried out according to UNI EN ISO 10545.4 and the values reported are the average of five samples.

Although the samples containing glasses have lower values than the reference, their mechanical properties are higher than those prescribed by the EN ISO standard for highly sintered commercial tiles (BIa group: WA≤0.5%, MOR>35 MPa) and can be considered as porcelain stoneware. The data of the compositions with the highest (20 wt%) glass content are not available (n.a.), as these samples showed very high porosity values compared to the standard. As porosity affects the mechanical properties, a further reduction in the value of the modulus of rupture was to be expected.

Other experiments investigate the effect of *TRE_PIN01* and *TRE_PIN02* in frits used for different ceramic tiles glaze formulations (glaze 1 and glaze 2). These formulations can contain up to 30% by of *TRE_PIN01* and *TRE_PIN02*.

In order to compare the effect of the presence of *TRE_PIN01* and *TRE_PIN02* in the glaze compositions with respect to the industrial standard formulation, solar reflectance (SR) measurements were carried out on the finished glazed tiles and characteristic temperatures were determined using a heating microscope. The expansion coefficient (EC) was determined by dilatometric analysis. The results are shown in (Table 8).

In both cases (incorporation of WEEE glass in support and glazes), the characterizations demonstrated the feasibility of the process and the substantial equivalence of the properties of standard and glass-based products. WEEE is a problem, but it is also a good opportunity to contribute to the self-sufficiency of the economic policy of those countries, such as Italy, that are poor in virgin or strategic raw materials.

This waste can be recycled and reused if it is managed effectively. Furthermore, improving the collection, treatment and recycling of the electronic equipment at the end of its life can increase resource efficiency and support the transition to a circular economy. It can also contribute to the security of supply of critical raw materials and ultimately strengthen the EU's strategic autonomy. The "PINECOR – ECO-efficient Integrated Process for WEEE Recovery" project aimed to develop innovative solutions capable of optimizing the recovery of glass and metal and siliceous fractions deriving from WEEE recycling.

Table 5. Chemical composition (wt% oxide) of TRE_PIN01 *and* TRE_PIN02 *glasses*

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	*MgO*	*CaO*	Na_2O	K_2O	SO_3	B_2O_3
TRE_PIN01	73.11	0.02	1.13	0.05	3.37	8.86	13.20	0.37	0.20	-
TRE_PIN02	72.52	0.02	2.06	0.04	0.79	8.34	12.11	1.05	0.15	2.81

Table 6. Characteristic temperatures and expansion coefficient *(EC) of* TRE_PIN01 *and* TRE_PIN02 *glasses*

	Glass transition (°C)	*Sintering (°C)*	*Softening (°C)*	*Sphere (°C)*	*Half sphere (°C)*	*Fusion (°C)*	*EC (1/K)*
TRE_PIN01	573	708	749	1028	1049	1079	$10.6 *10^{-6}$
TRE_PIN02	574	709	837	978	1064	1107	$10.5 *10^{-6}$

Table 7. Experimental values of water absorption (WA %), linear shrinkage (LS %), total porosity (TP %) and Modulus of Rupture (MOR, MPa) of WEEE glass containing support and standard support

	WA %	*LS %*	*TP %*	*MOR (MPa)*
Standard Support	0.003	7.49	7.41	64.16
2.5% TRE_PIN01	0.002	7.50	7.20	55.62
5% TRE_PIN01	0.001	8.02	7.45	50.39
10% TRE_PIN01	0.001	7.99	8.15	46.77
15% TRE_PIN01	0.0005	7.69	9.84	47.10
20% TRE_PIN01	n.a.	n.a.	n.a.	n.a.
2.5% TRE_PIN02	0.003	7.50	7.50	57.84
5% TRE_PIN02	0.001	7.86	7.83	53.66
10% TRE_PIN02	0.001	8.32	7.99	54.41
15% TRE_PIN02	0.001	7.19	8.90	47.76
20% TRE_PIN02	n.a.	n.a.	n.a.	n.a.

Table 8. EC, Characteristic Temperatures, Solar Reflectance (SR) values of standard formulations (STD) and respective WEEE-glass containing ones. Solar reflectance (SR) was measured according to ASTM C1549

	EC 10^7 1/K	*Softening temperature °C*	*Sphere temperature °C*	*Half sphere temperature*	*SR*
STD glaze 1	66	830	1030	1130	0.856
TRE_PIN01 containing-glaze 1	82	951	999	1084	0.853
STD glaze 2	66	830	1030	1130	0.740
TRE_PIN02 cointaining-glaze 2	65	828	1031	1127	0.754

The aim was to reduce waste and increase the recovery of secondary raw materials coming from the "dry mechanical treatment" of WEEE rich in glass free of toxic metal oxides, with high reuse potential, collected in groupings R1 (cold and climate), R2 (large whites), R4 (small appliances and other, including photovoltaic panels). The process used is integrated and eco-efficient, combining mechanical and chemical approaches to promote the reuse not only of the main fractions obtained from the recycling of end-of-life products, but also of the residues which are currently sent for disposal, which represents an additional cost. The partnership between the world of research (UNIMORE) and industry (TREEE srl, the leading Italian group in the WEEE sector, and TRE EFFE Forniture Idrauliche Industriali srl), and with the involvement of companies that have shown interest in the project, has allowed a continuous comparison between the academic and industrial worlds, which has materialized in the development of prototype of processes and products illustrated below.

The results obtained confirmed the multifunctional character of the PINECOR process; certainly, from a PINECOR perspective, shredding is a phase that should be included in the standard pre-treatment processes for WEEE. Furthermore, some intermediate fractions of the pre-treatment (such as the mixed plastics and metals from R4) require further research on the technology to reduce them to millimetres.

Glass from fridge shelf (*TRE_PIN01*) and washing machine (*TRE_PIN02*) has been used as a raw material both in the formulation of glazes and traditional ceramic supports and in the production of tiles for cool roofs (cold roofs with high reflectivity), which are designed to keep the building cool, counteracting the phenomenon of the so-called island of heat, as evidenced by the development of laboratory demonstrators. Semi-industrial trials are currently underway.

More problematic was the management of the mix of small household appliances (*TRE_PIN03*), a very heterogeneous sample which required a study of the separation of the different product fractions as a preliminary phase for the development of parallel recovery processes for the different product fractions obtained, in this case plastics and metals. Two physical separation processes were tested: separation by dense homogeneous liquids and elutriation. With regards the first, solutions of $ZnCl_2$, K_2CO_3 and NaOH were used to separate the materials by density difference: the $ZnCl_2$ 70% solution, in contact with 1 mm ground *TRE_PIN03*, gave the best results in terms of separation. However, the most effective process was elutriation, which allowed the separation of four different fractions of plastics and metals based on size, shape and density. The isolated metal fraction was then used to develop a process for the recovery of copper, a material for which this process is economically justifiable since it is present in non-negligible quantities in WEEE, through the development of an eco-sustainable chemical leaching process that does not use toxic or carcinogenic reagents and followed by deposition in the solid state through a galvanic process that can be carried out in the same leaching tank, thus maintaining the same chemical solution for both phases.

Regarding the plastic fraction, the following three fractions have been identified: light plastics for deep hole drilling such as polystyrene (PS), polypropylene (PP), polyethilene (LDPE and HDPE), styrene acrylonitrile (SAN); medium molecular weight plastics such as polypropylene (PP), acrylonitrile butadiene styrene (ABS); heavy plastics such as polycarbonate (PC), polyoxymethylene (POM), polyamide 6 (PA6).

With regards to the experimental phase for the recovery of the siliceous matrix, the initial project was aimed to use a widespread technology, considered to be "standard", which consists of treating the glass with sodium hydroxide using a pressurized reactor (25 bar), bringing the product to a minimum temperature of 220°C, with a minimum contact time (only in the peak phase of the reaction) of 2 hours. This type of treatment is already used in processes that are now industrialized at an international level.

Therefore, during the design phase, it was considered to test other less known methods, but more in line with the ecological transition now necessary aimed at researching more sustainable and safer technologies for both operators and the environment. The operational phase focused on pilot-scale tests carried out on an SPR (Shock Power Reactor) plant using the cavitation principle. Although the objective set was not fully achieved during this experimental phase, despite the diversification of the tests carried out, the treatment of glass with soda in the SPR reactor is a system on which studies and analyzes of the recovery variables of glassy matrices of WEEE origin will continue. However, the PINECOR project has made it possible to study many details and aspects that are inevitably an integral part of a technological evolutionary process.

Acknowledgements

This research was co-financed by Italian Ministry of the Environment and Energy Security in the call Co-financing of research projects aimed at developing new technologies for the recovery, recycling and treatment of electrical and electronic equipment waste (WEEE). 2020 Edition. Project title "PINECOR - Processo INtegrato ECO-efficiente Recupero RAEE (ECO-efficient and Integrated Process for WEEE Recovery). Project Cup: E93C20007890008

The authors thank Project stakeholders: SICER Spa - Raw materials and semi-finished products for the ceramic industry and Polis Manifatture Ceramiche Spa - ceramic floors and coverings.

References

AssoAmbiente, (2023), Recycling Italy, On line at: https://assoambiente.org/files/rapporto-italia-che-ricicla-2023.pdf.

CDC RAEE, (2018), Annual Reports (in Italian), On line at: https://www.cdcraee.it/wp-content/uploads/2021/08/rapporto-annuale-2018.pdf.

CDC RAEE, (2019), Annual Reports (in Italian), On line at: https://www.cdcraee.it/wp-content/uploads/2021/08/rapporto-annuale-2019.pdf.

CDC RAEE, (2020), Annual Reports (in Italian), On line at: https://www.cdcraee.it/wp-content/uploads/2022/03/CDC-RAEE-RA2020.pdf.

CDC RAEE, (2021), Annual Reports (in Italian), On line at: https://www.cdcraee.it/wp-content/uploads/2022/03/Rapporto-annuale-2021-pdf-1.pdf.

CDC RAEE, (2022), Annual Reports (in Italian), On line at: https://www.cdcraee.it/wp-content/uploads/2023/02/Rapporto-annuale-2022.pdf.

CDC RAEE, (2023a), Annual Reports (in Italian), On line at: https://www.cdcraee.it/wp-content/uploads/2024/03/rapporto-RAEE-nazionale.pdf.

CDC RAEE, (2023b), Annual Reports (in Italian), On line at: https://www.cdcraee.it/news/online-il-rapporto-gestione-raee-2023/.

Cheshmeh Z.A., Bigverdi Z., Eqbalpour M., Kowsari E., Ramakrishna S., Gheibi M., (2023), A comprehensive review of used electrical and electronic equipment management with a focus on the circular economy-based policy-making, *Journal of Cleaner Production*, **389**, 136132, https://doi.org/10.1016/j.jclepro.2023.136132

Endhoven T., (2023), European Construction Market Forecast to 2025, Ceramic Word Review, On line at: https://ceramicworldweb.com/en/economics-and-markets/european-construction-market-forecasts-2025.

EE Re P R, (2024), Erion- Ecodom Remedia Producer Responsibility, WEEE management investment plan, On line at: https://www.senato.it/application/xmanager/projects/leg18/attachments/documento_evento_procedura_commissione/files/000/308/401/Documentazione_ERION.pdf.

European Commission, (2020), A New Circular Economy Action Plan for a Cleaner and More Competitive Europe, Bruxelles, On line at: https://wbc-rti.info/object/document/20285.html.

European Commission, (2024), The Ecodesign of Energy-Related Products (ErP), On line at: https://joint-research-centre.ec.europa.eu/scientific-activities-z/sustainable-product-policy_en#:~:text=The%20Ecodesign%20of%20Energy%2DRelated%20Products%20(ErP)&text=It%20is%20estimated%20that%20over,design%20phase%20of%20a%20product.

Khan M.A.R., Motalib M.A., Saadat A.H.M., (2022), Mobile phone and spent laptop waste: generation, dissemination and flow pattern analysis, *Environmental Engineering and Management Journal*, **21**, 1339-1349.

Remedia and IEFE-Bocconi University, (2017), Challenges and prospects of the national WEEE management system, research report n. 30 (in Italian), On line at: https://green.unibocconi.eu/sites/default/files/media/attach/RR30%252BSFIDE%252BE%252BPROSPETTIVE%252BDEL%252BSISTEMA%252BNAZIONALE%252BDI%252BGESTIONE%252BDEI%252BRAEE.pdf

Serpe A., Purchase D., Bisschop L., Chatterjee D., De Gioannis G., Garelick H., Kumar A., Peijnenburg W.J.G.M., Piro V.M.I., Cera M., Shevahi Y., Verbeek S., (2024), 2002–2022: 20 years of e-waste regulation in the European Union and the worldwide trends in legislation and innovation technologies for a circular economy, *RSC Sustainability*, http://doi.org/10.1039/d4su00548a