Innovative approach for the valorization of useful metals from waste electric and electronic equipment (WEEE)

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Abstract: Waste electric and electronic equipment are an important secondary source of rare and precious metals and their processing through ecological technologies constitutes a major concern in the European Union and significantly contributes to the reduction of environmental pollution and to the preservation of valuable resources of nonferrous metals. The paper presents an innovative approach for the complex valorization of useful metals contained in WEEE. The method consists in the melting of WEEE in a furnace in a microwave field at temperatures of 1000 ÷ 1200°C, for the complete separation of the metallic fraction from the organic components. The gases resulting from the melting process were also treated/neutralized in a microwave environment and the obtained metallic bulk (multi-component alloy) was processed through combined hydrometallurgical and electrochemical methods. The major elements in the metallic bulk (Cu, Sn, Zn, Pb) were separated/recovered by anodic dissolution, respectively by leaching in nitric acid followed by cementation using various agents, or by electrodeposition. Depending on the electrochemical parameters, cathodic deposits consisting of Cu, with a purity higher than 99.9%, or of Cu-Sn and Cu-Sn-Zn alloys were obtained. Silver was valorized by leaching/precipitation with NaCl and the gold concentrated in the anodic slime will be recovered by thiourea extraction. The experiments performed demonstrate the possibility of ecological and efficient processing of WEEE in a microwave field and the recovery of nonferrous and precious metals through combined hydrometallurgical and electrochemical methods.

1. Introduction
The rapid technological advancement in the consumer electronics industry lead to the fast replacement of products, generating high amounts of electrical and electronic equipment waste, in the range of 20 to 50 million tones/year worldwide. Amongst WEEE, the printed circuit boards (PCBs) represent a very important source of nonferrous (Cu, Al, Fe, Ni, Pb), rare and precious metals (Au, Ag, In, Sr, Ta, etc.), but especially of Cu and Au [1, 2, 3]. The frame of the printed circuits represents approximately 23% of the PCB’s weight [4, 5]. The copper (20%) and gold (250 g/t) contents in a printed circuit board used in a common computer are much higher than those existing in an ore, respectively 20-40 times (Cu) and 25-250 (Au), times higher [4, 5]. Printed circuits are present in a wide range of
electronic equipment and small-sized home appliances: electronic instruments, toys, sports gear, etc. The frame boards have an inhomogeneous chemical composition and a complex structure, containing approximately 50÷55% organic components and 45÷50% metallic fraction.

As e-waste also contains toxic metals (cadmium, mercury, etc.) and organic pollutants such as flame retardants, their processing represents an important issue in respect to the EU environmental policies. WEEE processing for the recovery of the component metals is a subject which generated various studies and which also led to the development of technologies based on the combination of classical pyro- and hydrometallurgical methods for metals separation/obtaining. The most beneficial economical and environmental methods for treating and recycling electric and electronic equipment waste are the thermal techniques such as direct combustion, co-incineration with plastic wastes, pyrolysis and gasifying, after a previous treatment by physical-mechanical processes. Compared to the classical pyrometallurgical technologies for nonferrous metals waste processing, the melting in a microwave field is a modern and ecological process. The use of microwave energy for the melting of nonferrous metals wastes and for the treatment of resulting gases significantly reduces the reaction time of the treating process and implicitly the energy and fuel consumption.

In this context, the paper studies the development of an advanced technology for environment greening by innovative WEEE processing in a microwave field. After the microwave melting of the comminuted electronic wastes a multi-component alloy is obtained, which is subsequently treated by hydrometallurgical and electrometallurgical methods for the extraction of the constituent metals. The leaching of useful metals in the metallic bulk can be carried out in acid or alkaline media and in ionic liquids. Subsequently they can be recovered from the obtained solutions by a wide range of methods such as electrolysis, precipitation, cementation, absorption, ion exchange or solvent extraction. The most frequently used leaching agents are: HNO₃, aqua regia, NaOH, cyanides, halides, thiourea, thiosulfate, etc. [6, 7, 8, 9]. The majority of hydrometallurgical routes for processing PCBs use sulfuric acid leaching in the presence of H₂O₂ as oxidizing agent, followed by solution refining [1, 3, 9]. The use of nitric or hydrochloric acids was studied intensively, but because of the environmental regulations and the corrosive nature of these leaching agents they are as appropriate as the less hazardous sulfuric acid [10].

Electrometallurgical methods for processing PCBs present the advantages of reducing the reagent consumption and of an increased recovery efficiency for valuable metals and they have a mitigated impact on the environment [11, 12, 13]. The studied electrochemical processes for the recovery of base metals from PCBs are based on two major steps which can be carried out in a single cell: 1) the anodic generation of oxidizing agents for increasing the rate of metal dissolution; 2) the cathodic electrolysis of the dissolved metals for separation and recovery.

2. Experimental

2.1. WEEE melting in microwave field

The electronic wastes used in the experiments came from the dismantling and grinding of printed circuit boards (PC, radio, TV, mobile phones, etc). The comminuted material was melted in a microwave field in inert atmosphere (Ar). Microwave melting presents a series of advantages, such as rapid heating cycles with energy savings of approximately 35%, compared to conventional melting methods; an improved process control; no direct contact with the heating materials; the possibility of processing various nonferrous metals containing wastes (WEEE, Al and brass, etc.) for the recovery of constituent metals with high efficiencies (94÷96% for the multi-component alloy). This innovative method allowed the complete and efficient separation of the metallic fraction and the organic components.

The printed circuit boards were grinded down to sizes of approximately 0.5÷2 cm and melted in an experimental installation, in the following conditions:
- Three microwave generators of 800 W capacity each, placed circularly on the furnace casing;
- Working temperatures of 1000÷1200°C;
- Temperature measurement using a Pt/Pt-Rh wire thermocouple;
- Time: approx. 30 minutes;

The technological flow-chart is presented in figure 1.

![Figure 1. Technological flow-chart of the WEEE microwave melting.](image)

The experimental melting installation is composed from the steel casing, on which three microwave generators are placed outwardly (figure 2). The microwave susceptor silicon carbide crucible, in which the metallic waste is placed, is situated inside the furnace.

![Figure 2. Microwave melting furnace: 1- Microwave generator; 2 – Furnace casing; 3 – Thermal insulation; 4 – Layer of microwave susceptor material; 5 - Crucible; 6 – Thermocouple; 7 – Furnace lid; 8 – Raw material (WEEE).](image)

For eliminating the heat loses through the chamber walls, a thermal insulation (3) layer fabricated of superaluminous ceramic fiber, which can resist to temperatures of up to 1600°C, is inserted between the exterior wall of the crucible (5) and the furnace chamber (2). The material is heated using three microwave generators (1) of 800 W capacity each, mounted on the furnace walls. Flux (NaCl+KCl mix in a 1:1 ratio) is added to diminish the risk of metal oxidation during melting, in an amount which represents 5-10 wt% of the waste quantity. The chemical composition of the resulting multi-component alloy, cast as ingots, is given in table 1.

![Table 1. Chemical composition of the multi-component alloy.](image)

| Element | Cu | Sn | Pb | Zn | Fe | Ni | Al | Ag | Au | Other* |
|---------|----|----|----|----|----|----|----|----|----|--------|
| %       | 55-70 | 10-20 | 5-15 | 5-10 | 0.5-2 | 0.5-3 | 0.5-4 | 0.5-0.8 | 0.05-0.2 | 0.3-1 |

*Other: Sb, Mn, Mo, Cr, Ti, V, Ta
2.2. Multi-component metallic bulk processing
The technological flow-chart of the multi-component metallic bulk processing is given in figure 3.

![Technological flow-chart of the multi-component metallic bulk processing.](image)

For the study of the leaching in acid and ionic liquid media, metallic bulk fragments were ground in a ball mill. The particle size distribution of the ground alloy is given in table 2 and figure 4.

| Sieve opening | < 0.5 mm | 0.5 | 1 | 2 | 4 |
|---------------|----------|-----|---|---|---|
| %             | 30-32    | 20-25| 28-30| 9-12| 5-8 |

![Particle size distribution of the grinded WEEE.](image)

The dissolution process was carried out using nitric (HNO₃) and sulfuric (H₂SO₄) acids and ionic liquids based on choline chloride (ChCl).

The acid leaching experiments were carried out in a 2 liter 3 neck round bottom flask. The flask was heated with an electric heater and the temperature was controlled using a mercury thermoregulating thermometer. A water-cooled condenser tube was used to reduce the solution loss by vaporization and to reintroduce the solution in the reaction vessel. Using this installation design the solution losses were less than 50 ml. Heated compresses air was injected through a glass tube which
was inserted in the place of the agitator and which was in contact with the metallic material. The experimental installation for the acid leaching of WEEE is presented in figure 5.

![Figure 5. Leaching installation: 1. Leaching reactor (3 neck flask); 2. Electric heater; 3. Vapor condenser; 4. Mechanical agitator; 5. Mercury thermo-regulating thermometer; 6. Glass tube for hydrogen peroxide injection.]

The silver contained in the obtained nitric solutions was precipitated as insoluble AgCl with the addition of sodium chloride (0.6 g NaCl/g Ag). The silver chloride was subsequently separated through filtering and dried in an oven. Metallic Ag was obtained by melting the dried AgCl in an electric furnace, using a ceramic crucible and adding a Na$_2$CO$_3$-coke mixture as flux.

The solutions obtained after the acid dissolution of WEEE were cemented using iron, zinc and aluminum. The experiments took place in 250 ml Berzelius beakers, at room temperature and employing a 400 rpm agitation speed. The pH value of the cemented solutions ranged between 1.5 and 2 and was corrected with NaOH (2M). The quantities and shapes of the metals used for cementation are listed in table 3.

| Cementing metal | Fe | Zn | Al |
|-----------------|----|----|----|
| Quantity [g/g/l Cu] | 1.0 | | |
| Shape | Scrapings/lathe chips, 0.1-0.2 mm | |

For the anodic dissolution experiments a parallelepipedic anode was machined from the metallic bulk. The obtained anode was 100x60x5 mm in size and weighted 250 g. The process was performed in a 1500 cm$^3$ tank, using two stainless steel working electrodes (70x60x0.5mm) which were placed symmetrically towards the anode. The anodic connection was established with a copper wire. A MOS QJ 3020E current source (0-30V and 0-20 A) and a FALCO F70 magnetic heater-stirrer were used in the experiments. The electrochemical installation is presented in figure 6. The dissolution was carried out in an acid electrolyte composed of 200 g/l H$_2$SO$_4$, 120 g/l CuSO$_4$ x 5H$_2$O (Cu content of 30g/l) and 2 g/l brightening agent, at a temperature of 60°C. The potential was maintained in the range of 0.35-0.4 V and the current density was set at a constant value of 0.02 A/cm$^2$. The process was carried out until the complete dissolution of the WEEE anode, which was achieved after 200 hours. Samples were taken periodically from the electrolyte, anodic slime, cathode deposit and anode to determine the evolution of the chemical composition, which was analyzed using a Spectroflame P inductively-coupled plasma spectrometer.
3. Results and discussion

The chemical compositions of the solutions which resulted after the leaching of electronic waste are presented in tables 4 and 5. The Cu leaching rates for the ionic liquids used are given in table 6. Copper leaching efficiency is significantly higher in the case of nitric acid. This is caused by the presence of the NO$_3^-$ ion which acts as a strong oxidizing agent. An addition of hydrogen peroxide is required to increase the leaching efficiency when sulfuric acid or ionic liquids are used. The WEEE leaching in ionic liquids was complete in 0.2M CuCl$_2$•2H$_2$O +30% ChCl after the addition of H$_2$O$_2$ (30%) as catalyst, reaching a Cu dissolution rate of 100% (table 6).

Table 4. Chemical composition of the solutions obtained from WEEE leaching in HNO$_3$ (4 M), [g/l].

| Element | Cu | Sn | Pb | Zn | Fe | Ni | Al | Ag | Other* | Cu leaching efficiency, % |
|---------|----|----|----|----|----|----|----|----|---------|---------------------------|
|         | 55-65 | 0.01-0.4 | 7-10 | 7-9 | 0.2-0.4 | 0.5-0.8 | <0.2 | 0.7-1.2 | <0.0002 | 0.1-0.4 | 91 - 96 |

*Other: Sb, Mn, Mo, Cr, Ti, V, Ta

Table 5. Composition for solutions obtained from WEEE leaching in H$_2$SO$_4$ (2M)+H$_2$O$_2$, [g/l].

| Element | Cu | Sn | Pb | Zn | Fe | Ni | Al | Ag | Other* | Cu leaching efficiency, % |
|---------|----|----|----|----|----|----|----|----|---------|---------------------------|
| without H$_2$O$_2$ | 5-8 | 0.2-0.3 | <0.003 | 2-3 | 0.1-0.2 | 0.2-0.3 | <0.04 | <0.001 | <0.0001 | 0.1-0.5 | <16 |
| with H$_2$O$_2$ | 10-12 | 0.2-0.5 | <0.03 | 2-5 | 0.5-2 | 0.2-0.5 | <0.04 | <0.001 | <0.0001 | 0.1-0.5 | 18-22 |

*Other: Sb, Mn, Mo, Cr, Ti, V, Ta

Table 6. Leaching rate of the ionic liquids used.

| Ionic liquid (IL) | Molar ratio | IL type | Cu leaching efficiency, [%] |
|-------------------|-------------|---------|-----------------------------|
| ChCl-Urea         | 1:2         | DES*    | ~ 90                        |
| ChCl-Malic acid   | 1:2         | DES     | ~ 90                        |
| ChCl- Ethylene glycol | 1:2         | DES     | ~ 95                        |
| 0.2M CuCl$_2$•2H$_2$O +30% ChCl | - | analog | 100 |

* Deep eutectic solvent

After the precipitation in HNO$_3$, the silver content exhibited a major decrease from an initial value of 0.7-1.2 g/l to a value lower than 0.01 g/l. The chemical composition of the Ag obtained after the melting of the precipitated and dried AgCl is given in table 7.

Table 7. Chemical composition of the Ag obtained from the melting of the precipitated AgCl.

| Element | Cu | Sn | Pb | Fe | Ag |
|---------|----|----|----|----|----|
| % wt    | <0.003 | <0.001 | <0.002 | <0.003 | rest |

One approach for the recovery of copper from the WEEE was cementation with iron, aluminum and zinc as precipitant metal. Cementation is the precipitation of a metal by other metals which are
more electropositive. This process has been used extensively in hydrometallurgy for recovering valuable metals from all sorts of industrial wastes. An important aspect of this process is the use of metals which are already present in the solutions, avoiding contamination with other ions.

The general reaction of the cementation process is equation (1):

\[ \text{Cu}^{2+} + Me = \text{Cu} + Me^{2+} \quad (1) \]

where Me is the cementing metal.

The chemical compositions of the cemented solutions and of the resulting cements are presented in tables 8-13. The evolution of the copper content in the cementation process is shown in figure 7.

Table 8. Chemical composition of the nitrates and sulfates solutions cemented with Fe [g/l].

| Element | Cu   | Sn  | Pb  | Zn  | Fe  | Ni  | Al  | Other |
|---------|------|-----|-----|-----|-----|-----|-----|-------|
| Nitrates| 18-22| <0.1| 7-10| 1.5-2.4| 40-50 | 0.5-0.8| <0.1| <0.1 |
| Sulfates| 0.1-0.8| <0.1| <0.001| 1.5-2.5| 8-18 | <0.1| <0.1| <0.1 |

Table 9. Chemical composition of the nitrates and sulfates solutions cemented with Zn [g/l].

| Element | Cu   | Sn  | Pb  | Zn  | Fe  | Ni  | Al  | Other |
|---------|------|-----|-----|-----|-----|-----|-----|-------|
| Nitrates| 30-35| <0.1| 7-8 | 45-50| <0.1| 0.5-0.6| <0.1| <0.1 |
| Sulfates| 0.8-1.5| 0.1-0.3| <0.01| 30-34 | 0.1-0.3| 0.1-0.2| <0.01| <0.1 |

Table 10. Chemical composition of the nitrates and sulfates solutions cemented with Al [g/l].

| Element | Cu   | Sn  | Pb  | Zn  | Fe  | Ni  | Al  | Other |
|---------|------|-----|-----|-----|-----|-----|-----|-------|
| Nitrates| 0.2-1| <0.1| 4-6 | 5-6 | 0.2-0.4| 0.4-0.5| 20-25| <0.1 |
| Sulfates| 0.1-0.5| <0.1| <0.001| 0.5-1.5 | 0.3-0.8 | 0.1-0.5| 18-20| <0.1 |

Table 11. Chemical composition of the Fe cements.

| Element | Cu   | Sn  | Pb  | Zn  | Fe  | Ni  | Al  | Cu leaching efficiency, % |
|---------|------|-----|-----|-----|-----|-----|-----|---------------------------|
| Nitrates| 97-99.5| 0.1-0.2| 0.1-0.2| 0.01-0.05| 0.4-1| 0.2-0.8| 66-68 |
| Sulfates| 60-99.5| 0.5-4| <0.001| 0.1-0.3| 0.1-40| 0.5-1.2| 93-99 |

Table 12. Chemical composition of the Zn cements.

| Element | Cu   | Sn  | Pb  | Zn  | Fe  | Ni  | Al  | Cu leaching efficiency, % |
|---------|------|-----|-----|-----|-----|-----|-----|---------------------------|
| Nitrates| 90-94| 0.1-0.4| 0.5-0.8| 3-5 | 0.1-0.2| <0.2| 35-45 |
| Sulfates| 92-95| 0.1-0.3| 0.3-0.6| 4-6 | <0.1| <0.2| 87-91 |

Table 13. Chemical composition of the Al cements.

| Element | Cu   | Sn  | Pb  | Zn  | Fe  | Ni  | Al  | Cu leaching efficiency, % |
|---------|------|-----|-----|-----|-----|-----|-----|---------------------------|
| Nitrates| 85-90| 0.01-0.05| 4-5 | 0.01-0.05| 0.2-0.4| 0.01-0.05| 5-15| 97-98 |
| Sulfates| 60-99.5| 0.5-4| <0.001| 0.1-0.3| 0.1-40| 0.5-1.2| <0.01| 92-98 |

It can be observed that for the sulfate solutions with initial Cu contents of 10-12 g/l the average cementation efficiency is higher than 90%. In the case of the nitrate solutions, the highest efficiency (>90%) is attained when Al is the cementing metal, whereas in the case of Fe and Zn the cementation efficiencies are approximately 60% and 40%, respectively. A possible explanation for this phenomenon could be the re-dissolution of the copper containing cements in the excess of HNO₃.

These results lead to the conclusion that cementation may be used successfully for purifying the solutions resulting from the nitrate and sulfate leaching of electronic equipment waste and the recovery of copper.
The results of the anodic dissolution process are given in tables 14, 15 and 16, which present the chemical compositions of the electrolytes used in the anodic dissolution process, of the cathodic deposit and of the resulting anodic slime.

**Table 14.** Chemical composition of the electrolytes after the anodic dissolution process.

| Element | Cu | Sn | Pb | Zn | Fe | Al | Ag | Au | Other |
|---------|----|----|----|----|----|----|----|----|-------|
| g/l     | 2-6| 12-20| <0.1| 8-15| 0.5-2| 0.1-0.3| <0.001| <0.001| 0.1-0.3 |

**Table 15.** Chemical composition of the cathode deposit vs. the current density.

| D_K [Acm⁻¹] | Element | Cu   | Sn   | Zn   | Pb   | Al   | Fe   | Ni   | Other |
|--------------|---------|------|------|------|------|------|------|------|-------|
| 0.02         | wt.%    | 99.5-99.8 | <0.1 | <0.01 | <0.01 | <0.01 | <0.01 | <0.1 |
| 0.06         |         | 87.0-95.0 | 5-10 | 0.02-0.1 | 0.1-0.5 | <0.02 | <0.01 | <0.1 |
| 0.1          |         | 60.0-65.0 | 25-30 | 0.8-1.2 | 0.8-1.5 | 0.2-0.5 | <0.1 | 0.5-0.8 |
| 0.2          |         | 30.0-35 | 58-65 | 1-1.2 | 0.5-1.5 | 0.1-0.5 | 0.1-0.2 | 0.6-0.8 |

**Table 16.** Chemical composition of the anodic slime.

| Element | Cu   | Sn   | Pb   | Zn   | Fe   | Al   | Ag   | Au   | Other* |
|---------|------|------|------|------|------|------|------|------|--------|
| wt.%    | 5-8  | 25-30 | 40-48 | 0.2-0.5 | 0.2-0.5 | <0.1 | 4-6.5 | 0.6-1.5 | 1.2-1.5 |

*Other: Sb, Mn, Mo, Cr, Ti, V, Ta

From the data presented in table 14 it can be observed that the copper contents decreased significantly after the electrodeposition. In table 15 and in figure 8 it can be observed that the purity of the copper deposits decreases as the current density increases. The highest Cu content is obtained when the dissolution takes place at a current density of 0.02 Acm⁻¹. In general, the electrowinning process is characterized by a significantly higher efficiency in the case of sulfate electrolytes compared to nitrate solutions. This is caused by the presence of the NO₃⁻ ion in nitrate electrolytes, which reduces the efficiency of the metal extraction through electrolysis.
4. Conclusions
This paper demonstrated the technical feasibility of an innovative method for the recovery of useful metals contained in electronic waste. The WEEEs were processed through a combined pyro-hydro-electrometallurgical approach. The melting in a microwave field allowed the complete and efficient separation of the metallic fraction and the organic components and also an efficient treating of the resulting gases. The major elements in the resulting metallic bulk (Cu, Sn, Zn, Pb) were extracted by leaching in nitric acid followed by cementation using Fe, Al and Zn or by electrochemical deposition. The leaching of the metallic bulk carried out in different ionic liquids demonstrated that the best electrolyte for the complete alloy dissolving is a mixture of 0.2M CuCl$_2$$\cdot$2H$_2$O +30% ChCl. Anodic dissolution seems to be the most efficient technological approach for the separation/recovery of the useful metals. Cathodic deposits consisting of Cu (purities >99.9%) or Cu-Sn and Cu-Sn-Zn alloys were obtained in the anodic dissolution process, depending on the electrochemical parameters. The highest Cu content was achieved when the dissolution was carried out at a current density of 0.02 Acm$^{-1}$. Precious metals were also valorized: silver was recovered by precipitation with NaCl and the gold was concentrated in the slime which resulted from the anodic dissolution process.

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