

Selective recovery of valuable metals from crushed electronic waste

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Abstract: This research was carried out to recover valuable metals from the electronic waste (e-waste). E-waste samples were crushed and thermally activated under 450 °C within 1 hour. The optimal temperature of the thermal treatment, at which all organic phases are removed and metal's forms turned into oxides was determined. Leaching of thermally activated material using EDTA at room temperature, pH 7 for 1 hour resulted in greater than 95 % extraction of lead. Non-ferrous metals were extracted at 85 °C with a leaching solution of 2 M H₂SO₄ which resulted in recovery of more than 98 % of copper within 3 hours.

1. Introduction

The electronic waste (e-waste) is an attractive source of raw materials for the extraction of non-ferrous, precious and rare metals. According to [1, 2], there is about 20-50 % by weight of copper and other valuable components, including Pb, Sn, Zn, Al, Ag, Au, Pd, etc. are contained in the e-waste depending on the type of device.

There are various methods for the e-waste recycling well known today, which in the majority are based on the combination of pyrometallurgical, hydrometallurgical and electrometallurgical technologies [2, 4, 5].

Hydrometallurgical routes for the e-waste processing are described by a high degree of recovery of the target components (Cu, Zn, Pb and precious metals), by a flexible mode of operation and by the possibility of application on a small scale. These factors make hydrometallurgical processes more economically stable for processing a wide range of the e-waste, including low-grade ones. Nevertheless, there is no existing technology for the e-waste recycling, completely based on hydrometallurgical processes on an industrial scale.



Different acids could be used as the leaching agents for metals extraction from the e-waste - sulfuric acid, nitric acid, hydrochloric acid and their mixtures [6, 7]. Basically, during the leaching process several metals are simultaneously dissolute in the solution (Cu, Pb, Zn, Sn etc.), which leads to the further difficulties on the step of the re-extraction of metals from productive solutions. Considering this point, the authors of this article recommend to conduct the e-waste leaching in stages using different leaching agents for the selective extraction of metals.

Methods for the selective extraction of oxidized forms of lead from industrial products using various organic solvents (alkylamines) are given in several published works [8, 9]. One of the main advantages of leaching with organic solvents is the possibility of separation of Pb and Ag. Authors [9] also note that the use of ethylenediaminetetraacetic acid (EDTA) for lead leaching from industrial products of zinc production allows the selective separation of Pb, Cu, Zn and Fe^{n+} .

The main purpose of this research was to experimentally confirm the possibility of the recovery of valuable metals from the e-waste via physical pre-treatment, thermal treatment and chemical treatment (leaching with different solutions).

2. Experimental procedures

2.1. Materials and methods

The samples used in the experiment were printed circuit boards (PCBs) and automobile microcircuits weighed to a specified mass, sourced from various waste computers and automobiles regardless of brand. Component analysis of the PCBs used in this experiment determined the metal component to be 53 % by weight, and this consisted of base metals (Cu 32.87 %, Fe 5.49 %, Ni 0.69 %, Sn 3.55 %, Pb 2.05 %, Al 5.50 %, and Zn 2.44 %) and precious metals (Au 5.1 g/ton, Ag 1346 g/ton, and Pd 182.7 g/ton). Plastic materials were 20 % by weight and consisted of more than 16 % C-H polymers, which included polypropylenes and α -polypropylenes; less than 4 % halogenated polymers (mainly polyvinyl chloride (PVC), traces of polytetrafluoroethylene (PTFE), and polybromo compounds); and less than 1 % N-containing polymers, including nylon and polyurethanes. Also, metal oxides were 27 % by weight and included 11 % silica, 4.5 % alkaline and alkaline earth oxides, 4 % alumina, and 7.5 % other oxides.

To extract valuable metals, Pb was dissolved in EDTA solution (crystalline powder dissolute in water), Cu, Fe, Zn, Ni, and Sn were dissolved in H_2SO_4 (98 %, extra pure (EP) grade). Di-(2-ethylhexyl) phosphoric acid (DEHPA) was used to selectively extract Zn^{2+} and LIX extraction agent and kerosene were used in combination to selectively extract Cu^{2+} from SO_4^{2-} solution.

2.2. Experimental setup

Figure 1 shows a flowchart for the recovery of valuable metals from the e-waste samples, developed in the framework of this research. The e-waste samples were firstly shredded by plastic cutter “Scutter SA-22 (Stolz Co., Ltd)” and then crushed by a disc mill. Crushed e-waste samples were sorted by size using a sieve that allowed only pieces within 0.08-0.25 mm to pass through. Pieces larger than 0.25 mm were crushed again to a suitably smaller size and re-sieved.

Crushed materials were thermally treated in a laboratory muffle furnace SNOL 7,2/1100 at temperature range 400-450 °C. The time of the thermal treatment of the sample (1 hr) was determined according to the differential scanning calorimetry (DSC) results, which correspond to the rate of oxidation of the organic components. The thermally treated materials were used as the source from which valuable metals were extracted.

The leaching experiments were carried out in heat-resistant fluoroplastic beakers with capacity of 500 ml equipped with a pH meter, a top-drive electrical laboratory stirring device “IKA RW 16 basic” set at 500 rpm, and a condenser in a thermostatically controlled water bath. Analyses of components of the starting material were carried out using an atomic absorption spectrometer (AAS) and inductively coupled plasma-mass spectrometer (ICP-MS).

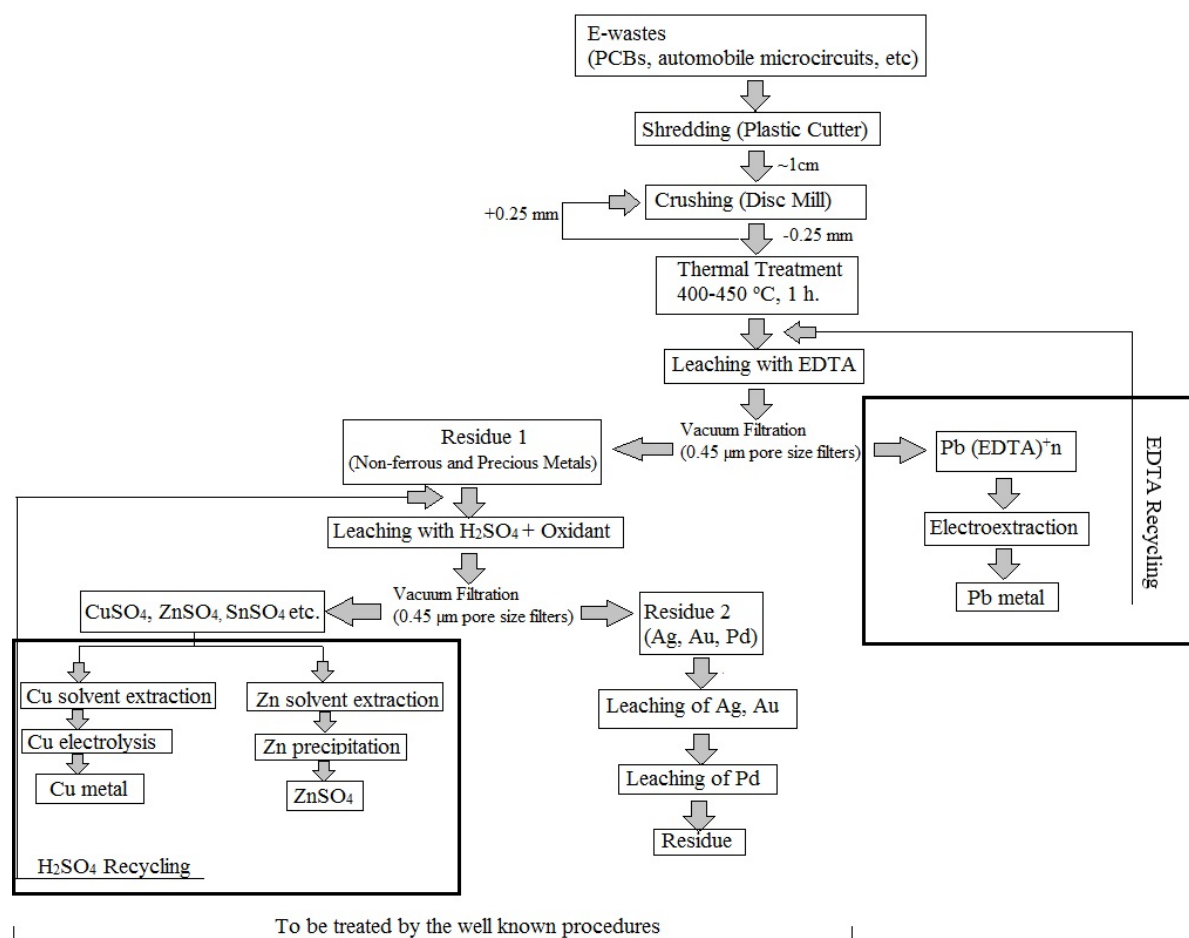


Figure 1. Flowchart for the recovery of valuable metals from the e-waste.

3. Results and discussion

3.1. Thermal treatment effect

The crushed materials (average particle size of 0.08-0.25 mm) were thermally treated in the laboratory muffle furnace SNOL 7,2/1100. The efficiency of the thermal treatment was investigated using the synchronous thermal analyzer Mettler Toledo for the thermo-gravimetric analysis (TGA) and DSC.

Laboratory tests of the thermal treatment of the starting material were conducted in the temperature range 25-700 °C to determine the temperature zone of the complete removal of organic phases from the e-waste materials. The process time in the furnace was determined by the rate of oxidation of organic components, based on the results of DSC, and was 1 hour. It was found that the maximum percentage of the removal of organic phases is observed in the temperature range 400-450 °C.

Phase analysis of the material after the thermal treatment at 450 °C showed the presence of oxide forms of Pb, Cu and Zn, etc. At the same time, the content of all valuable metals after the thermal treatment increased by 25 % by mass of the e-waste, including: Cu (41 %); Pb (2.56 %); Zn (3 %); Ag (1750 g/ton); Au (12.5 g/ton). TGA-DSC analysis results of the thermally activated material are presented in Figure 2.

The formation of the metals' oxide forms as a result of the thermal treatment makes possible to conduct at the next stage the leaching process with EDTA for the selective Pb extraction.

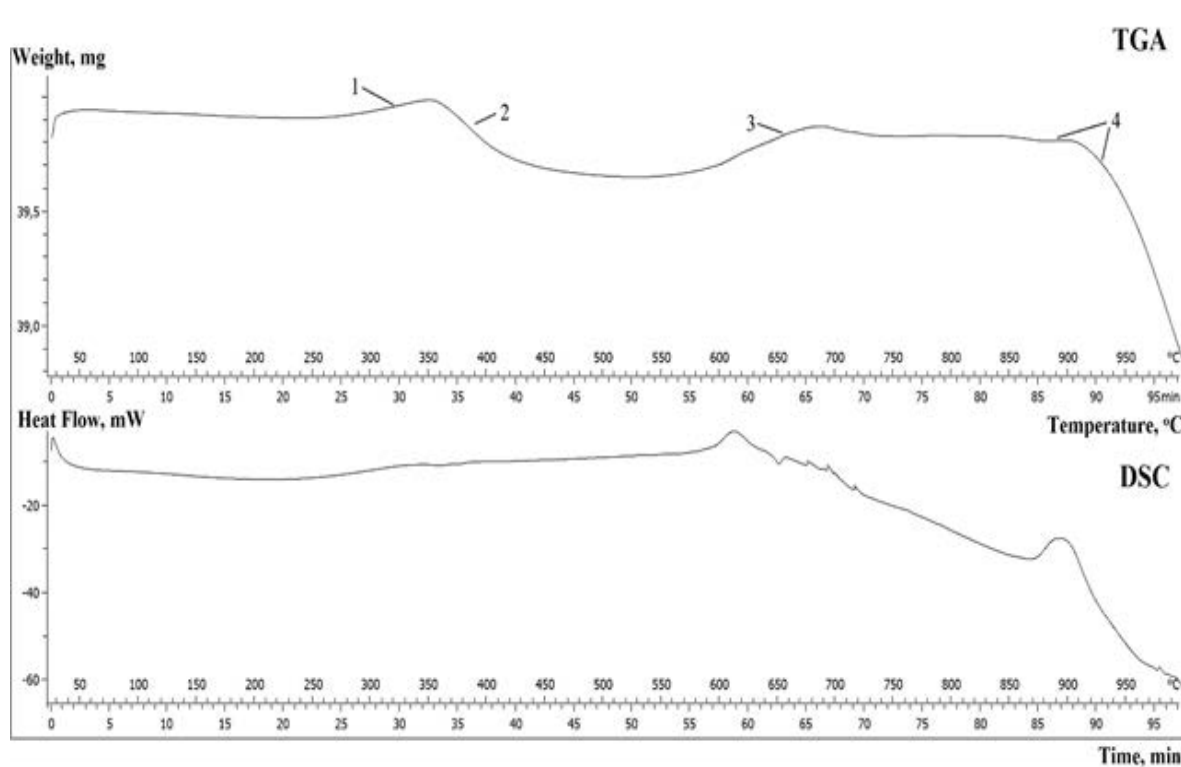


Figure 2. TGA and DSC curves of the thermally activated e-waste in air atmosphere, heating rate $10\text{ }^{\circ}\text{C}, \text{min}^{-1}$. TGA curve: 1 - weight increase by 0.19 %; 2 - weight loss by 0.84 %; 3 - weight increase by 0.55 %; 4 - weight loss by 2.47 %.

3.2. Selective Leaching of Pb with EDTA

Authors [10] investigated that EDTA selectively forms complex compounds with cations of non-ferrous metals in different pH ranges and the strength and solubility of the formed metal complexes depend on the pH and density of the solution.

Complexing reagent EDTA (concentration of 100 g/l) was used as the leaching solvent to selectively extract Pb oxide forms from the crushed thermally activated e-wastes. Leaching experiment was carried out at $25\text{ }^{\circ}\text{C}$ and 60 min. An aqueous solution of caustic soda (concentration of 200 g/l) was supplied in order to achieve and maintain a predetermined pH value. pH was maintained constant during the experiment process, dosing the required volume of alkali (NaOH).

In order to investigate effects of pH and solution's density on the Pb (EDTA)_n complexes formation, experimental tests for different pH (5; 7; 10) and density values (liquid-solid ratio: 3:1; 7:1; 10:1) were carried out. Productive solutions after leaching with EDTA was filtered through 0.45 micron filter using a system of vacuum filtration. Residues were dried overnight and analyzed by X-Ray fluorescent analysis to determine content of Pb, Cu and Zn. Figure 3 shows the extraction rates of these three metals in different pH, while Figure 4 shows the effect of density (liquid-solid ratio) on the leaching of the metals with EDTA.

The optimal conditions for EDTA leaching were found to be a solution 100 g/l EDTA, pH – 7, L:S ratio 10:1 and a reaction temperature of $25\text{ }^{\circ}\text{C}$, which achieved 92-95 % selective extraction of Pb within 1 hr, while Cu and Zn remained in the residue.

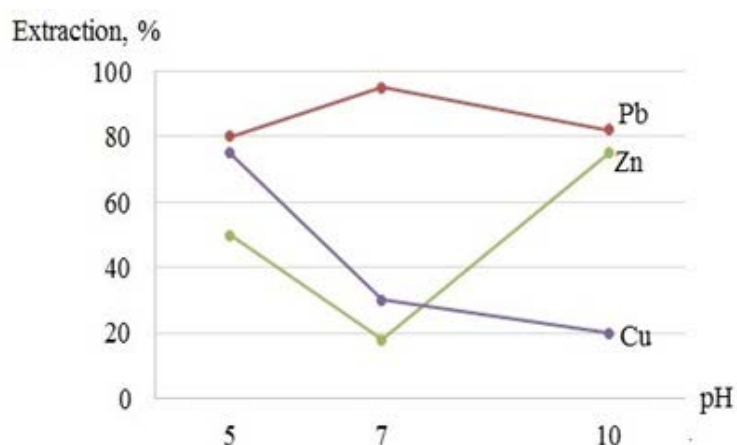


Figure 3. Dependence of metals extraction in the solution on the pH value at 25 °C and liquid-solid ratio (L: S) - 10:1.

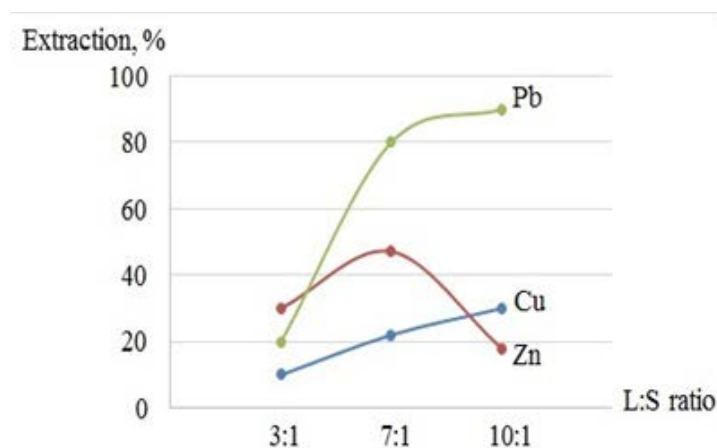


Figure 4. Dependence of metals extraction in the solution on the L:S ratio at 25 °C and pH 7.

3.3. Leaching of Metals with H_2SO_4

Sulfuric acid was used as the leaching solvent to extract the base metals, with air oxygen as an oxidant. The aeration of the system was achieved using a glass tube and an aquarium pump. The remaining solid material was filtered through 0.45 micron filter using a system of vacuum filtration, washed and leached in the next stage. Leaching with the H_2SO_4 solution was carried out at 40, 65, and 85 °C over a period of time. The H_2SO_4 concentration ranged from 0.5 to 2 M, 10 g of sample per L of leaching solution were added.

The main target component at the H_2SO_4 leaching stage is copper, because of its high content in the sample (32.87 %). In order to optimize the leaching parameters, 3D surface characterizing the dependence of copper extraction in the solution on the temperature and leaching time (see Figure 5a) and 3D surface characterizing the dependence of copper extraction on the temperature and H_2SO_4 concentration (Figure 5b) were constructed applying the program STATISTICS 10.0.

The optimal conditions for H_2SO_4 oxidative leaching were found to be a solution 2 M of H_2SO_4 and a reaction temperature of 85 °C, which achieved ~ 98 % recovery of Cu within 3 hr.

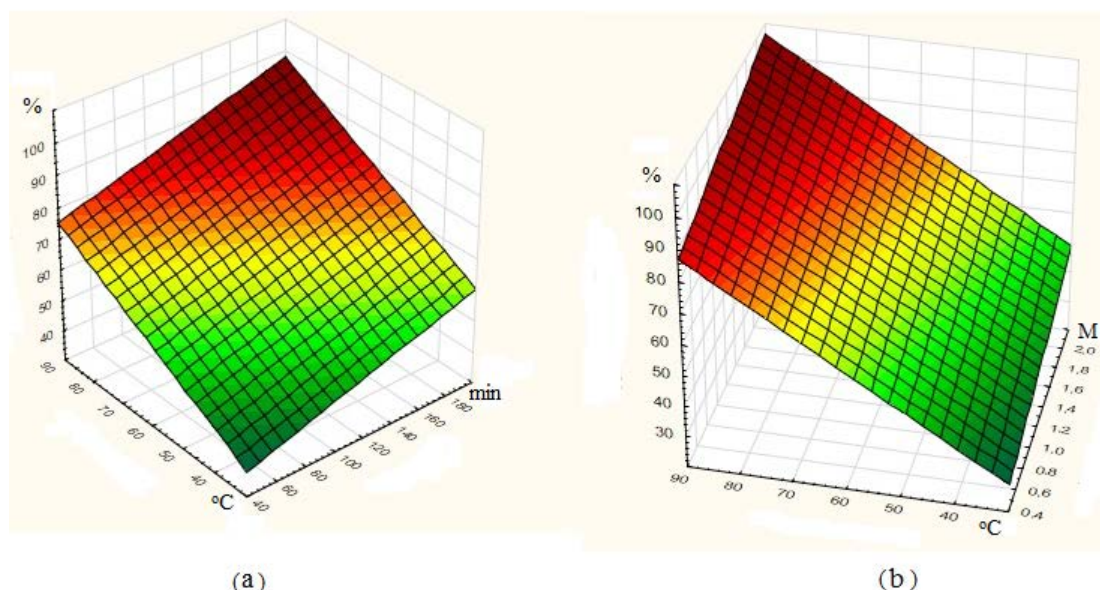


Figure 5. (a) Dependence of copper extraction to the solution (%) on the temperature ($^{\circ}\text{C}$) and leaching time (min); (b) Dependence of copper extraction to the solution (%) on the temperature ($^{\circ}\text{C}$) and H_2SO_4 concentration (M).

4 Conclusions

The present research developed a leaching procedure for the recovery of valuable metals from e-wastes via physical pre-treatment, thermal treatment and chemical treatment, and the results at each stage are as follows.

(1) The results of the thermal treatment showed that the maximum percentage of the removal of organic phases and formation of the metals' oxide forms are observed in the temperature range 400–450 $^{\circ}\text{C}$. Presence of metals' oxide forms makes possible to conduct further step of the leaching with EDTA for Pb selective extraction.

(2) In the leaching reaction using 100 g/l EDTA at 25 $^{\circ}\text{C}$, pH 7, L:S - 10:1, 95 % of Pb was selectively leached out within 1 hr.

(3) In the case of leaching with the leaching solution of 2M of H_2SO_4 solution at a reaction temperature of 85 $^{\circ}\text{C}$, 98 % of Cu was leached out within 3 hr.

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